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THE GENERATION OF SOUND BY THE SIREN PRINCIPLE

BY E. SIMEON

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ABSTRACT. The paper discusses various undesirable features of the simple siren, considered as a sound-source for technical work, and describes a siren with a reasonably pure note, whose intensity can be kept constant throughout a range of pitch from about 70 to about 7500 cycles.

THE production of a steady note at good strength is quite a simple matter, but to range over six or seven octaves with any certainty as to relative intensity is a good deal more difficult. The air siren (assumed to have a drive independent of the pressure air) seemed to promise well, on the assumption that the intensity (energy) of the sound will be some definite fraction of the input air energy, which is easily measured. In the simple type of siren, by reason of the resonant cavities and the light construction generally and also of a pump-action due to the revolving disc, this result can hardly be counted on, but by suitable design it is possible to remove the sources of error more or less completely, at the same time improving the wave-form and lengthening the useful frequency band at both ends.

Inside the usual air chest, waves from front to back set up by the escaping puffs must always be present to some extent, and may have a choking effect at some frequencies. By employment of a shallow chamber the effect might be avoided within the pitch range under consideration; the absence of an adequate reservoir would, however, both spoil the wave-form and also set up pulsations in the supply pipe to the detriment of some or all of the lower notes.

The best plan appeared to be to construct a push-pull or double siren and mount it on a large baffle board, the sound being radiated half to the front and half to the rear in opposite phases. The total hole area open at any instant would thus, with suitable choice of hole shapes as described later, be a constant. The need for a reservoir would disappear: the air would flow smoothly up to the point where it divided to the front and back sets of holes, the two sets being in close proximity. The rear radiation, together with any driving noises, would, of course, be kept away from any instrument under test.

The mechanical difficulties in the twin-rotor arrangement are greater than would be expected, and finally the principle shown in Figs. 1 and 2 was adopted. It employs the usual single rotor. Half or more of the output is lost, the remainder, however, being quite adequate for the purpose. In the trial siren of Fig. 1 the stationary front holes are drilled round in sets of three, adjacent sets being in opposite phase and on opposite sides of the separating fin; the latter serves to turn the unwanted sound to the rear as before. In Fig. 2 the stationary holes are in twos, an arrangement less liable to damp high frequencies, since it brings the opposite sets closer together. In passing, it is suggested that the push-pull construction might render more practicable the under-water, hydraulically blown siren. The simple type of siren appears actually to have been tried for submarine signalling, and to have failed to give satisfaction from some cause. Certainly the heavy and incompressible nature of water, as compared with air, calls for radical departure from the conventional design.

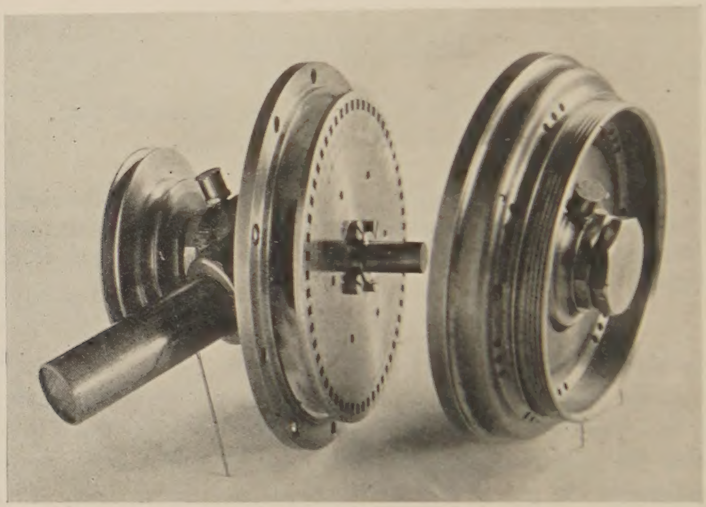

Fig. 1. Trial form of siren.

Something may be said on the question of wave-form. It has been pointed out* that for a pure note the flow of air should be controlled sinusoidally, e.g. by a disc with a continuous sine curve cut round the edge, the air under constant pressure issuing from a narrow radial slit. The unsatisfactory pointed wave-form with equal circular fixed and moving holes was also shown, and a special hole shape worked out. In the present case the hole dimensions cannot exceed about $\frac{1}{8}$ inch, as the peripheral velocity is quite limited; the only practicable shapes are the circle, ellipse, rectangle, etc. The width of moving and fixed holes must evidently be equal, for if one were smaller, no change in the air-flow would occur as it passed within the larger, so that a flat part would occur in the wave-form. For a similar reason the inter-hole width must be equal to the hole.

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* E. A. Milne and R. H. Fowler, *Proc. R.S.* A **98**, 414 (1921).

Fig. 3 shows how the effective area changes during the travel with a pair of equal circular holes, and with one circular and one square hole the same width, the direction of travel being perpendicular to a side. The wave-form with the latter is quite a good imitation of sine form (shown dotted); it is also symmetrical about the half-open line, a necessary condition if the two phases are to dovetail and draw air smoothly from the supply. Owing to the inclined drilling introduced in the design, the shape of the stationary holes becomes elliptical, and the rotor holes are accordingly made rectangular. The wave-form is not affected. The actual air flow resulting is probably not quite proportional to these aperture areas, as the holes are so small; at the same time the wave-form should remain much the same at any frequency. In other words, the relative strength of unwanted harmonics will not vary, and they can generally be neglected. The ear readily detects some departure from tuning-fork purity with the siren of Fig. 1; its workmanship was, however, only indifferent.

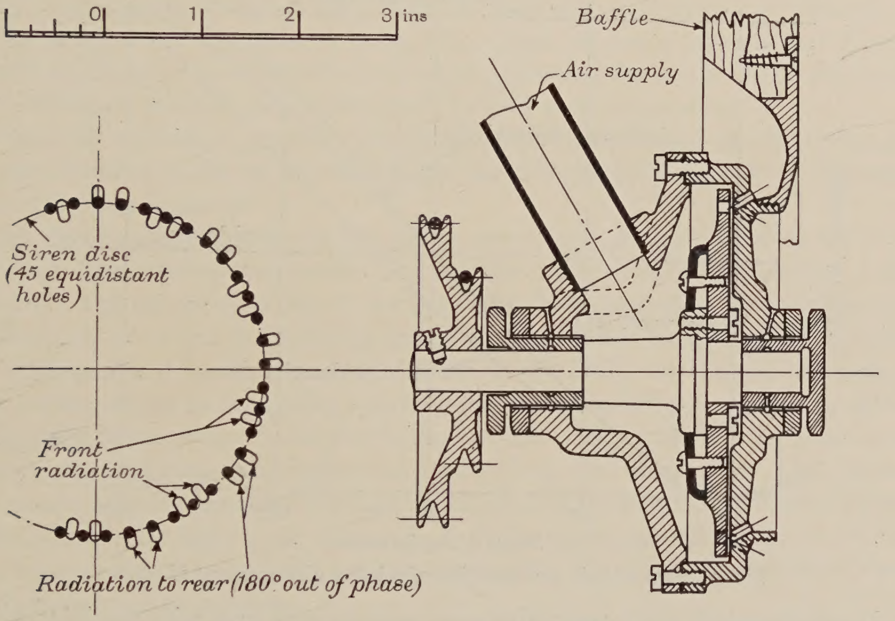
0
1
2
3 ins
Baffle
Air supply
Siren disc (45 equidistant holes)
Front radiation
Radiation to rear (180° out of phase)

Fig. 2. Final form of siren. Left: diagrammatic view showing drilling of front. Right: longitudinal section.

When the rotor is running at speed it naturally sets up a swirl of air in the case, and this adds something to the pressure on the holes. If the air be free to enter and flow through, a weak note can be produced in this way on all but the lowest part of the frequency range. The pressure actually existing at the inner end of the fixed holes may be measured if a short connection be made between two opposite phase holes in the front, and thence to the pressure gauge. This pressure, in ordinary testing, will be only an inch or two of water; the low part of the range naturally seems weaker to the ear, and may need more pressure, but a rushing of the air begins to be audible with about four inches. For the determination of the air energy the volume per second is also required. A holder of one to two cubic feet makes a good source of air, and if it be placed at the edge of the baffle there is no danger of sound pick-up.

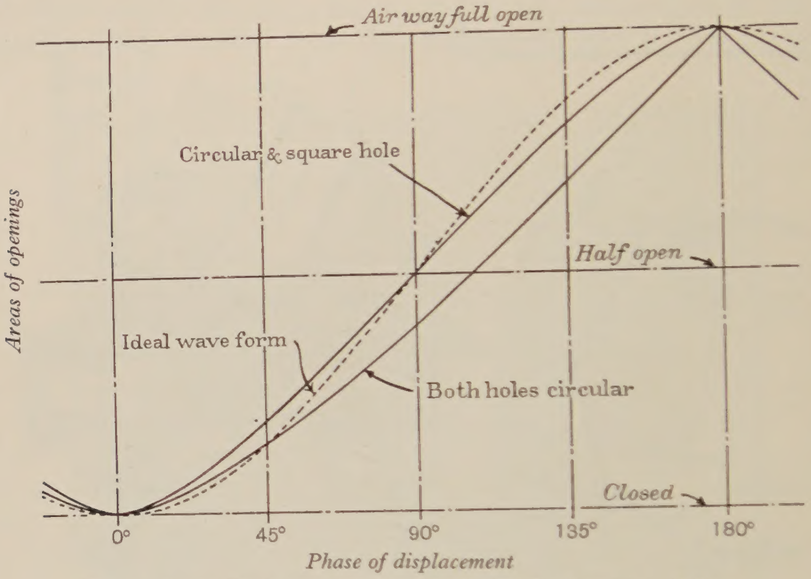

Fig. 3. Area of hole as a function of relative displacement of discs.

It may be noted that a very faint note can be heard even with the inlet and all joints effectively sealed. It is too weak to be of much consequence, so long as small working intensities be avoided at the higher frequencies. It seems to be due to a feeble air-flow from one side of the baffle to the other through both sets of holes, and must be put down to an accidental slope of one set towards the direction of motion, or the fact that one set slopes outwards and the other inwards.

A point of some uncertainty (which, however, applies to some other sources of sound) concerns the distribution of the different frequencies in front of the siren mounted on its baffle. The positions in which tests can be made are confined to the central axis, the appreciable dimensions of the siren relative to short wave-lengths leading otherwise to interference. If the low notes tend to spread out more rapidly than the higher, as seems possible, a source of error will be introduced in testing over a considerable pitch range. The effect, if present, could be detected by the taking of a few measurements with any good class microphone at low, medium and high frequencies, and repetition of the process farther out along the axis. If then found necessary, a correcting factor could no doubt be arrived at in some way.

A few notes on the construction may be added. When the trial siren of Fig. 1 was made it was thought that a speed of 7500 r.p.m. was as much as could be expected from a pulley drive. More recently, however, a different apparatus fitted with a pulley similar to the smaller one on the siren and a $\frac{1}{8}$ in. leather belt ran light at over 13,000 r.p.m. As compactness is very desirable a smaller rotor is shown in the design of Fig. 2 (pitch diameter 3·44 in. with 45 holes and spaces, each 0·12 in. across) to run up to 10,000 r.p.m., or 7500 cycles per second. To avoid distortion it is made from annealed mild steel. A damping disc with paper washer is screwed to it to discourage vibration, and for the same reason the case is substantially made.

The lower pitch limit is rather undefined. A musical tone is distinguishable down to 35 cycles, though a very large baffle would be required to preserve the fundamental at full strength. A baffle 6 ft. square is clumsy enough, but this size should be adequate down to about 70 cycles, provided the test point be not too far out. Owing to the low speeds, it is hard to hold these notes steady.

Open air working is generally preferable; but if a deadened chamber were employed the siren could be mounted in an aperture in the wall, and the unwanted sound dissipated outside.

As already suggested, the purity of the note depends a great deal on the workmanship. The placing and width of the holes ought to be accurate, well within 0·002 in. For the siren of Fig. 1 the rotor disc, and later the front casting, were attached to a plate and the dividing was carried out at five times the drilling radius. All drilling was done through hard bushings in an arm rotating pointer-fashion. The drilling of the sloping holes proved difficult, particularly as regards the setting in opposite phase of the two sets of holes, but this work would be simplified by the slightly altered form of the baffle attachment shown in the drawing. One cause of inaccuracy was the breaking through of the drill at an angle underneath, where a waste disc should have been fastened. A faint raggedness noticeable in the tone may be traced to the hand-filing of the rectangular rotor holes, a procedure hardly good enough for its purpose.

DISCUSSION

Dr A. B. Wood: Mr Simeon is to be congratulated on a very nice piece of work. Both the design of the siren and the actual construction are excellent. The point of particular importance is, of course, the introduction of the artificial load (the rearward holes) between the intervals of useful sound generation (by the forward holes). This should result in a greatly improved smoothness of running of the siren.

With regard to the wave form: presumably Fig. 3 illustrates the theoretical wave form. I should very much doubt, however, whether this will be found to agree with the observed wave-form. It seems to me that the amount of high-pressure air escaping through the overlapping orifices at any instant will depend not only on the area of the combined opening but also on the periphery and general shape of the opening. Eddies at the edges of the opening are bound to have an important influence on the wave-form of the sound generated by the siren. This criticism will apply also to the siren devised by Milne and Fowler.

As Mr Simeon remarks, the fundamental principle of his improved siren might also find an application to a water-siren. The general design would, however, require radical alteration for such use. A siren for signalling in the sea was designed during the war by Sir Charles Parsons. This was driven by high-pressure water and gave ranges of several miles. Difficulties of a practical nature proved to be rather serious and precluded its general use as a submarine signalling device.

Mr R. W. Hardisty: I should like to congratulate Mr Simeon on a most interesting paper on the subject of a device, which, if the claims made for it can be substantiated, will be of great service to workers in applied acoustics.

Telephone engineers have been paying much attention recently to the improvement of the frequency/response curves of carbon microphones as applied both to the ordinary subscriber's telephone instrument and to studio transmitters used in broadcasting stations. Carbon microphones must always be calibrated in an open sound field, and the need for a device with a constant sound-output in any particular direction is acute, owing to the non-linear distortion present in many microphones of this type.

The only available source at present is the loudspeaker which is generally of the moving-coil type; and, as is well known, the frequency-response curves of all loudspeakers are far from linear and are moreover liable to change with atmospheric conditions. These changes produce very considerable errors in the resultant frequency characteristics of microphones.

I should like to ask the author if he has made any measurements of the acoustic output of the device at a point distant about 4 or 5 ft. from it. The output from sirens is quite large as a rule and, as Dr Thomas pointed out when reading the paper, the wave-form could have been improved by utilising only half the width of the orifice. Such an improvement might be desirable for the purpose considered where a sound pressure of only about 5 dynes/cm.^{2} is required.

Author's reply: I must thank Dr Wood and Mr Hardisty for their kind remarks. As Dr Wood suggests, it is unlikely that the wave-form is actually as good as that indicated in Fig. 3, which only pretends to deal with orifice areas. The form would be further degraded by mechanical errors, such as certainly exist in the trial siren. Nevertheless, from experience with the latter I think one could obtain a note quite as pure as that of the flute, for example. Obviously further experiment is required, and this would incidentally show whether the wave-form does remain approximately the same at all frequencies. The question is an essential part of the whole problem, as one could not properly apply the push-pull principle with a definitely asymmetrical wave-form.

The original suggestion as regards under-water sirens has been slightly revised. I imagine that the difficulties ought not to be insuperable, but am totally ignorant on the subject.

No satisfactory measurements of the acoustic energy have yet been obtained, owing to the great difficulty of the process, particularly with limited resources.

With air continually streaming from the siren the Rayleigh disc cannot very well be used; the only method seems to be that employing a calibrated microphone in the open air. Once tested, the siren ought to hold its calibration well, especially if the rotor were made of some tough rustless alloy. The rectangular holes might be produced by milling in from the edge, and shrinking on an outer ring.

The paper is not put forward without apologies for its incompleteness; but some of the sound-sources that have been suggested seem so questionable that one gains confidence in proportion.

I cannot conclude without thanking Dr Thomas for his very kind help and interest on this and many other occasions.

SURFACE RESISTIVITY MEASUREMENTS ON SOLID DIELECTRICS

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ABSTRACT. The paper describes (1) a new form of electrode suitable for surface resistivity measurements on insulating materials in sheet form, and (2) a method for the determination of the "volume leakage" correction for any system of electrodes. Data are given on the volume leakage correction for the various types of electrode in general use, and on the "leakage resistivities" of materials commonly used in the construction of laboratory instruments.

§ 1. INTRODUCTION

Most electrical measuring-instruments are provided with terminal fittings mounted on a small panel of a solid dielectric, such as ebonite, bakelite, amber, ivory, or fused quartz. None of these materials is a perfect insulator, and it is found that in many cases the imperfection of the insulation is largely due to the passage of leakage currents over the surface of the material, rather than through its bulk. Accordingly, the measurement of the surface resistivity of materials of this kind is of some importance.

The usual method of measurement is to apply two conducting electrodes to the surface of the material, arranging them so that their nearest edges are parallel and a definite distance apart, 1 cm. say, and then to measure the total leakage current flowing when a known voltage is applied to them. Two difficulties arise: that of ensuring that the electrodes make good contact with the insulating material along their entire length, and that of estimating the leakage current which flows through the body of the material and is measured along with the surface current. A form of electrode that has been found to be very satisfactory for such measurements will now be described, and also a method for determining the correction to be made on account of volume conductance.

§ 2. THE ELECTRODES

An important series of measurements of surface resistivity has been made by Curtis*. His electrodes consisted of metal strips 1 cm. wide which were clamped to the sample (a piece 10 × 10 cm. cut from a flat sheet of the material) as shown in Fig. 1. The difficulty with this arrangement is that the strips bend, and so make good contact at the edges of the sample only. To get over this difficulty, Curtis wrapped the strips round with tinfoil, and pressed this against the insulator along the inside edge of each strip. This process will give satisfactory results but it is difficult to be quite certain that the contact has been made good enough. The arrangement used by the writer is shown in Fig. 2, which shows one electrode in elevation. The sample, shown shaded, is clamped between two stiff brass bars *A* and *B*, the pressure being applied in the first place by the wing nuts at the ends. Between each of the clamping bars and the insulating material there is a flexible strip of brass about 3 mm. thick, and these strips are pressed into contact with the sample by the set screws shown. The set screws are tightened in turn, until it is seen that the flexible strips, which are the real electrodes, make good contact with the sample over its entire length. A recess is cut in the face of each electrode, as shown in the end view in Fig. 2, so that contact is made not over the whole face of each strip but along the edges only, an uncut rim 1 mm. wide being left for this purpose. This arrangement improves the contact along the edges of the strips, where it is most important, and at the same time reduces the total area of contact, thereby diminishing the correction due to volume leakage. These electrodes are

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* *Bulletin of Bureau of Standards*, **11**, 359 (1915).

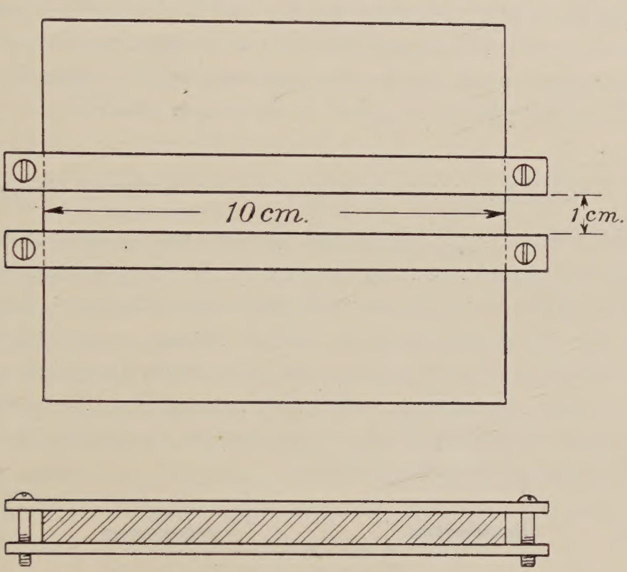

Fig. 1. Brass strip electrodes.

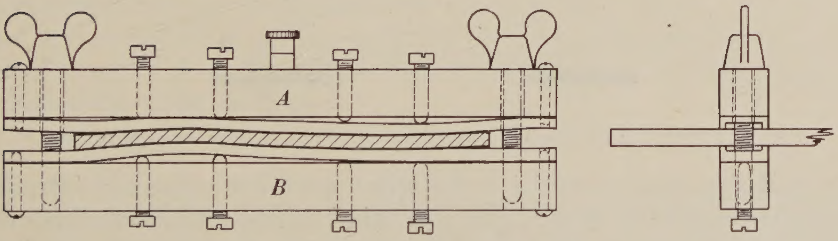

Fig. 2. The new form of electrode.

specially useful for dealing with samples which are neither flat nor of uniform thickness. Fig. 2 is greatly exaggerated in this respect in order to show the principle more clearly. Mere inspection of a sample in these electrodes is sufficient to show that the contact is good over the entire length. The degree of contact was also found to be reproducible; the same sample inserted in the clamps several times gave results differing by about 5 per cent., which was well within the probable experimental error due to temperature change and to the handling of the sample.

Good contact can also be obtained by the use of electrodes of mercury, and of graphite in various forms. The brass clamps have an important advantage over these for surface resistivity measurements; they are less likely to contaminate the surface to be tested. The manipulation required is also much easier.

§ 3. THE VOLUME RESISTIVITY CORRECTION

Whatever the nature of the electrodes applied to the surface of an insulator, there will always be current flowing from one to the other through the body of the material, and this must be measured with the surface current. Separation of the two currents is physically impossible in surface leakage measurement, although it is a comparatively simple matter to measure the volume resistivity alone by use of the well-known guard-ring arrangement. The volume resistivity being known, the correction on surface resistivity measurements can be determined for any system of electrodes by the method described below.

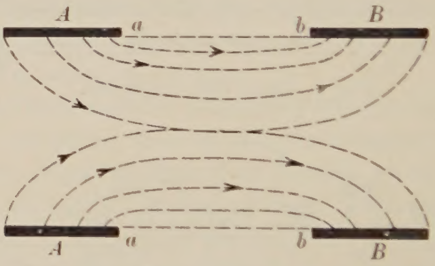

Fig. 3. Lines of electrostatic force or lines of flow of volume leakage current.

Let *A*, *B* (Fig. 3) be electrodes on the upper and lower surfaces of a flat sheet of insulating material. The dotted lines represent the lines of current-flow through the body of the material when a p.d. is applied between *A* and *B*, and the configuration of these lines determines the "volume resistance" of the arrangement. Now this configuration is the same as that of the lines of electrostatic force which will traverse the corresponding volume if the same electrodes be completely surrounded by a perfect dielectric medium. It follows that, if the volume resistivity be known, it is possible to determine the volume resistance by means of measurements of the capacity of similar electrodes, embedded in a medium of known dielectric constant. The case of the new electrodes described above will be considered as an example.

The standard sample is 10 × 10 cm., and thus the contact areas of the electrodes i.e. the effective electrodes) consist of strips 10 cm. long and 1 mm. wide. A model of these electrodes was made by the cementing of strips of tinfoil on to pieces of ebonite 10 × 10 cm. The strips representing the upper and lower parts of the electrodes were placed on separate pieces of ebonite, so that by the placing of a third ebonite piece of any desired thickness between them, a model of the electrode applied to a test piece of this particular thickness was obtained. All the pieces of ebonite measured 10 × 10 cm. and the tinfoil electrodes were always surrounded by ebonite at top and bottom. This is important since the arrangement must be symmetrical with respect to the plane of the electrodes if the correct field distribution is to be obtained. The symmetry ensures that the shortest line of force joining the two electrodes lies in the plane of the electrodes and thus corresponds to a line of flow of the surface leakage current (*ab* in Fig. 3). The electrode-model was now connected to a capacity bridge and its capacity measured for various thicknesses of sample from zero to 11 mm. It is obvious that the difference between the capacity for zero thickness and for, say, 1 cm. thickness, will give the capacity corresponding to the required field distribution in the sample 1 cm. thick. The leads connecting the model to the bridge are the same in every case, and all the external capacities are unaltered by the changing of the sample. Thus the capacity required is easily measured with a probable error of, say, 0·02 $\mu\mu$F.

The method* of measuring small capacities has already been described, but for these measurements no elaborate precaution is needed as all the usual errors cancel out when differences are taken. If C is the capacity in $\mu\mu$F of the required field in a medium of dielectric constant ϵ, then the corresponding volume resistance of a sample of volume resistivity ρ, is given by

$$R = \frac{\epsilon}{3{\cdot}6\pi C}\rho.$$

The most convenient way of expressing the correction is as follows. Let σ_a be the apparent surface resistivity of the sample, i.e. the value obtained when the volume resistivity correction is neglected. Let σ be the true surface resistivity, and ρ the volume resistivity. Then we have

$$\frac{1}{\sigma} = \frac{1}{\sigma_a} - \frac{\alpha}{\rho},$$

where α is the correction factor. This factor has been determined by the above method for the new electrode, for brass strips 1 cm. wide as used by Curtis†, and for the circular system of electrodes now widely used, in which the upper surface of the sample carries two electrodes, a circle surrounded by an annular ring concentric with it and separated from it by a gap across which the surface resistance is measured. The lower surface of the sample in the latter case carries a circular electrode of the same diameter as the upper ring electrode. For the surface resistivity measurement, the upper circle should be raised to a high potential. The ring should be connected to the current-measuring instrument, while the lower electrode should be earth-connected. In this way the bottom electrode acts as a partial shield for the ring electrode and reduces the volume-leakage correction. In the determination of the correction for this electrode-system the above conditions were satisfied, i.e. the capacity between the upper circle and the ring was measured, the capacities to the bottom electrode being eliminated by connection of this to earth*. In order to obtain a capacity measurement corresponding to zero sample-thickness in this case, a single sheet of tissue paper (thickness 0·02 mm.) was inserted between the upper and lower electrodes. This was sufficient to insulate these electrodes without separating them by an amount detectable by capacity measurements of this kind.

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* *Proc. Phys. Soc.* **36**, 399 (1924).

† *Loc. cit.*

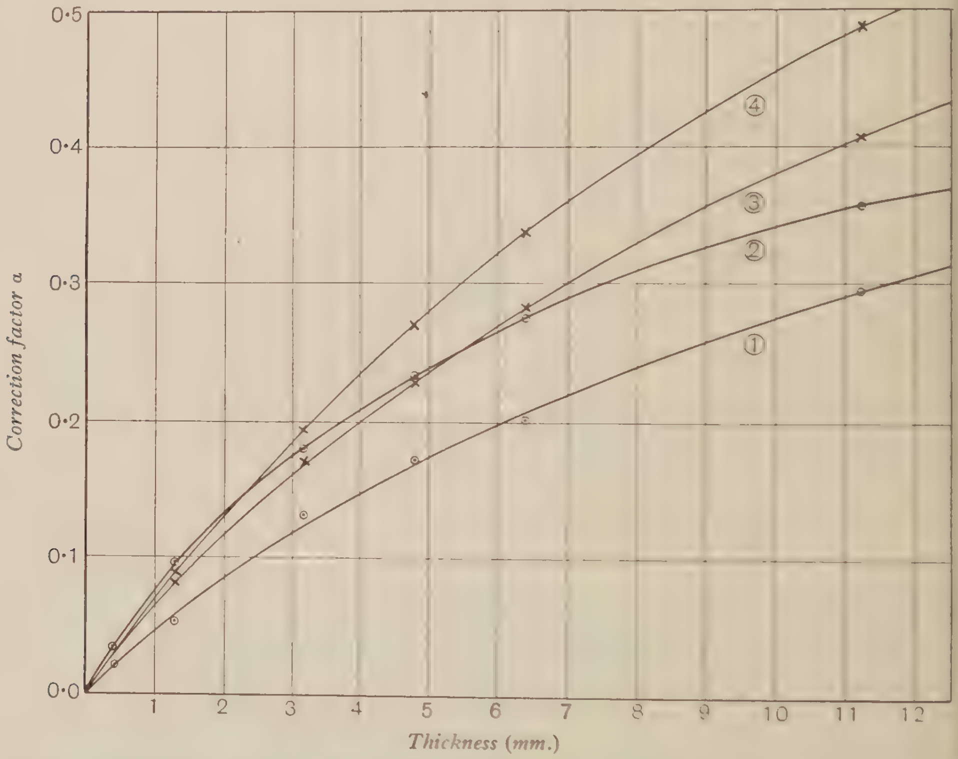

Fig. 4. The correction factor for volume conductance as a function of the thickness of the sample, (1) for the new electrodes 1 cm. apart; (2) for circular electrodes with a gap of 5 mm. and radii of 10, 10·5 and 15 cm.; (3) for plain brass strips, 1 cm. wide and 1 cm. apart; (4) for circular electrodes with a gap of 1 cm. and radii of 10, 11 and 15 cm.

All the results are shown in Fig. 4. It will be observed that the correction is least for the new brass clamps. From a consideration of the calculated capacity between strips infinitely wide on a sample 1 cm. thick, and strips 1 cm. wide on a sample infinitely thick, Curtis concluded that the correction for his brass strips was roughly one-third. The value now obtained is $0{\cdot}36_5$, which confirms Curtis' estimate.

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* *Proc. Phys. Soc.* **36**, 399 (1924).

It is evident from the general uniformity of the results in Fig. 4, that the cor-
ection for any system of electrodes can be read from this chart with all the accuracy equired for such work.

§ 4. RESULTS

An interesting series of results obtained by the use of the new electrodes escribed above is shown in Fig. 5. They are the outcome of an investigation under-
aken by Mr R. S. J. Spilsbury, of the Electrotechnics Department of the National hysical Laboratory, and the writer, in order to obtain data for the design of the erminal fittings of standard instruments. Two samples, 10 × 10 cm., were cut from in. sheets of each of the following insulating materials: high-grade ebonite (un-
oaded), bakelite, and keramot. The surface of one sample of each was polished, and

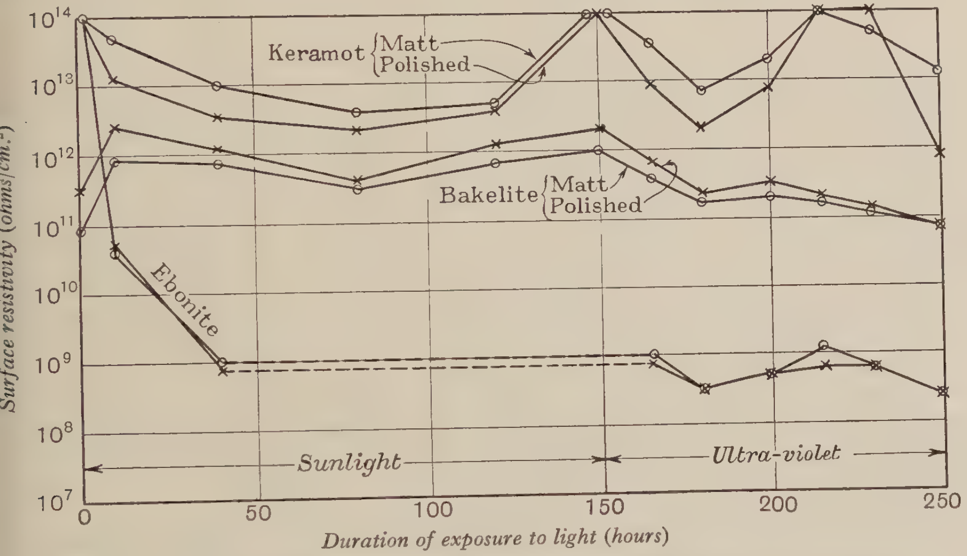

Fig. 5. Surface resistivity of insulating materials exposed to the action of light under ordinary atmospheric conditions.

the other was given the matt finish commonly found on instrument panels. Measurements of leakage resistivity* were made on each sample. They were then left in the ordinary atmosphere of a laboratory for several weeks and exposed to the action of light, at first sunlight (sometimes real, and sometimes artificial) and afterwards ultra-violet light from a mercury arc in quartz. Comparative measurements of leakage resistivity* were made at intervals. The applied p.d. was 200 volts and the current was measured with an ordinary moving coil galvanometer, so that resistivities greater than 10^{14} could not be measured. Initially, the values for ebonite and keramot were higher than this, but the ebonite deteriorated very rapidly. A comparatively slight deterioration of the keramot occurred at first, but it is evident that from the point of view of instrument design, the leakage resistivities of bakelite and keramot are unaffected by exposure to light, although the colour of the keramot fades. The changes of resistivity shown in Fig. 5 for keramot and bakelite are undoubtedly due to changes in atmospheric humidity. It is interesting to note that there is no very pronounced difference between the polished and matt surfaces of any of the materials. For bakelite the polished surface, i.e. the finish left by the manufacturers, is rather the better, but for keramot the reverse holds good. In the case of ebonite the results could not be distinguished.

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* A term, first used by Curtis, for the apparent surface resistivity uncorrected for volume leakage.

When it is remembered that the samples were inserted into the electrodes afresh for each measurement, the general consistency of the results for keramot and bakelite, in spite of fluctuating conditions, gives a good indication of the uniformity of the contact obtained with this type of electrode.

DISCUSSION

Dr H. A. Daynes: We have to thank Dr Hartshorn for a neat and practicable general method of estimating the volume leakage-correction and for a considerable improvement on the old type of brass-strip electrode. I should like to ask whether he has any quantitative data on the value of the contact resistance. I realise that it is difficult to obtain direct evidence of that kind but there might be some indirect evidence such as the extent to which the total resistance depends on screw pressure, or on the time elapsing after application of the pressure. It has been mentioned that the pressure is sufficient to impress tool marks on the specimen. Is it sufficient in the case of a matt sample to destroy the matt surface? One would expect that to be a necessary condition for perfect contact because if there is not perfect contact over the whole surface the resistance must be increased owing to local crowding of flow-lines.

With regard to alternative electrodes, it will be agreed that mercury is inconvenient to use and liable to contaminate the surface; moreover it does not always make good contact. I do not think the same can be said of graphite in all forms. Work has been carried out by the Rubber Research Association for several years on surface-deterioration of ebonite and a few years ago we introduced the use of "aquadag" as a means of applying a conducting electrode. Details will shortly be published in the *Transactions of the Institution of the Rubber Industry*. The colloidal water-suspension of graphite is painted or stencilled on and allowed to dry off. The adverse effect of the water disappears in about 2 hours. In our experience such an electrode is free from objection.

It may be mentioned that serious deterioration under the influence of sunlight does not take place with all qualities of ebonite. It is most marked with the purest qualities such as are required for very high dielectric strength and low dielectric loss at high frequencies. Where exposure to sunlight is inevitable, a better all-round performance can often be obtained by the use of an ebonite containing mineral and other ingredients, the trade product mentioned in the paper being one example of such compounded ebonite.

Dr L. Simons: In view of the fact that most rolled or cast materials have an effective skin in which the physical properties vary progressively with the depth, is the method adopted of correcting for the volume resistivity completely independent of such conditions? For example the capacity of the electrodes would be different when they are surrounded by a perfect insulator from what it is when the samples are sandwiched between dielectrics with surfaces exactly similar to those of the samples.

Dr J. H. Vincent: I congratulate the author on this important piece of work. Do the graphs in Fig. 5 indicate that keramot deteriorates at first and then recovers its high resistance?

Mr D. K. McCleery: I want to draw attention to the strong influence of atmospheric humidity on surface leakage. In certain tropical places where there is a damp and steamy heat, conditions are sometimes so bad that it is impossible to test without guard wires (I am referring to insulation tests of submarine cables). When guard wires cannot be used, a coating of paraffin wax on the surface has been found to give good results.

I should like to suggest the term "creepance" for the surface conductance.

Mr D. A. Oliver: I should like to express my admiration of the elegant method devised for determining the volume resistivity correction. It has enabled the measurement of the true surface resistivity to be placed entirely on an experimental basis. The results in Fig. 5 are of considerable practical interest, and bring out clearly that keramot—known already to possess good machining properties, a relatively small power factor and a coefficient of linear expansion not greater than ordinary ebonite—has the additional virtue of a high surface resistivity under ordinary atmospheric conditions. As corresponding values of volume resistivity are not given in the paper, would Dr Hartshorn give, for a typical case, some idea of the order of error likely to be introduced into a measurement of true surface resistivity by neglect of the volume resistivity correction?

Prof. C. L. Fortescue: Both physicists and electrical engineers are very much indebted to Dr Hartshorn for this work, because though the remarkable deterioration of ebonite and some other materials with exposure to light has been known for fifty or more years, no very exact measurements have been available. Now that these methods have been developed it is to be hoped that careful tests will be made of all the other materials available in place of ebonite, and that the results will be published.

Author's reply: I have no quantitative data on the actual contact resistance between the metal and dielectric surfaces, but the indirect evidence available is to my mind sufficient to show that such contact resistance is negligible in measurements made in the manner described in the paper. The applied mechanical pressure could of course be varied considerably by adjustment of the set screws, but once the proper contact was made, a further increase of pressure had no appreciable effect on the leakage current. Further, it will be observed that matt and polished surfaces of the same materials gave practically the same results in most cases. Thus even with matt surfaces the intimacy of contact was adequate. The results shown in Fig. 4 are evidence of the fact that perfect intimacy of contact, such as would allow for microscopic surface irregularities, is not necessary. For curve (3) the area of electrode contact was five times that for curve (1), whereas the volume leakage current is only greater by about 30 per cent. Thus with the degree of contact obtainable with the new electrodes, one could hardly hope to detect any increase of resistance due to local crowding of the lines of current flow at the contact surfaces.

The mechanical pressure was sufficient to impress tool marks on a polished ebonite surface, but not to destroy a matt surface. A polished ebonite surface takes an impression very easily, and was therefore used to test the uniformity of the contact along the length of the electrode.

I have used the graphite electrode described by Dr Daynes and believe it to be quite satisfactory for ebonite and similar materials. It does however demand careful manipulation. For testing new and unknown materials I prefer the brass electrode, because although the effect of applying water to an ebonite surface may disappear in two hours it does not follow that this would happen for all materials.

The volume leakage correction cannot be applied with accuracy to non-homogeneous materials of the kind described by Dr Simons. In fact such materials cannot be said to have a definite 'volume resistivity,' and any separation of the volume and surface leakage currents is purely arbitrary in such cases.

The apparent improvement noted by Dr Vincent in Fig. 5, is simply due to a diminution in atmospheric humidity.

The volume leakage correction is usually of importance only when measurements are made with a relative humidity less than 20 per cent. Curtis* has given data illustrating this point, and the following values of surface resistivity at low humidities are selected from his paper.

Bakelite,	uncorrected	10×10^{12},	corrected	30×10^{12}
Stabalite,	,,	5×10^{13},	,,	9×10^{13}
Amberite	,,	2×10^{15},	,,	2×10^{15}

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* *Bulletin of Bureau of Standards*, **11**, 415 (1915).

DIAMAGNETISM AND MOLECULAR STRUCTURE

Lecture delivered on November* 8, 1929, *by*
SIR C. V. RAMAN, F.R.S.

PHYSICISTS at the present day do not need to be reminded of the great importance of the subject of magnetism considered from the standpoint of chemistry, i.e. in relation to molecular structure. The subject of diamagnetism in relation to molecular structure, however, has not been so much to the fore as that of paramagnetism. At Calcutta we have approached the subject from a rather unusual standpoint in connexion with our investigations on the scattering of light. We were led to discuss the question how far it was possible to obtain a quantitative expression for the magnetic double refraction observed in liquids. I will remind you of a discovery in about 1912 by two French physicists—Cotton and Mouton†—who found that if they placed an organic liquid in a strong magnetic field H, Fig. 1, and observed the effect of the liquid on a beam of light L, passing through it transversely to the lines of magnetic force, certain liquids such as nitro-benzene showed a feeble double refraction, so feeble that it was at first only in very special classes of organic compounds, viz. benzene and its derivatives, that it was possible to observe it at all. Later on, improved methods of observation have extended very considerably the list of organic liquids in which this magnetic double refraction can be observed. These two French physicists also succeeded in detecting it in a very small number of aliphatic compounds, such as chloroform, bromoform, etc. and in a great many common liquids such as water and paraffins and the ordinary aliphatic hydrocarbons, ethers, alcohols, acids, etc. With some of the acids they were not able to observe the effect, and thus the great importance of the subject did not receive adequate attention.

Magnetic double refraction is exhibited by certain substances owing to their molecules possessing a magnetic susceptibility. That, of course, is obvious, but what is not quite so obvious is how exactly the magnetic double refraction arises.

About the time of the discovery by Cotton and Mouton there was already available certain work by Voigt‡, who showed that, as a consequence of the dispersion theory, if a beam of light passes through a substance placed in a transverse magnetic field, there must be a feeble double refraction produced; and this refraction was shown to be related to the Zeeman effect. You will find some reference to Voigt's work in his well-known book on magneto-optics published by Methuen.

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* Completed and revised, in the absence of the author, by J. S. G. Thomas, D.Sc.

† A. Cotton and H. Mouton, *Comptes Rendus*, **141**, 317–319 and 349–351 (1905).

‡ W. Voigt, *Gesell. Wiss. Göttingen Nachr. Math.-Phys. Klasse*, **2**, 215–220 (1913).

When Cotton and Mouton made their observations on magnetic double refraction in liquids they found that the actual effect observed by them was nearly 1000 times larger than what would be roughly estimated from Voigt's theory of the phenomenon. The consequence was that they realised that an entirely different explanation must be sought. Prof. Langevin was the first to suggest what is now fairly generally accepted as the real explanation of the effect*. I would like to make the thing clear by a little diagram, Fig. 1. If the incident light is plane-polarised and, in the absence of the magnetic field, is completely cut off by an analyser, suitably arranged, then we find that as soon as a transverse magnetic field is established there is a feeble restoration of light. This restoration is not a matter of the ordinary Faraday effect at all, as here we are dealing with light that is passed through a *transverse* magnetic field. The light has become elliptically polarised, and the ellipticity can be measured by suitable experimental methods. The idea, however, with which Langevin started was that the molecules of the liquid possess magnetic anisotropy. Langevin's theory has been developed by Born, who assumes that the molecules possess permanent magnetic moments and that in the condition of statistical equilibrium of the molecules in the magnetic field a small percentage of the molecules becomes preferentially oriented. The magnetic field only acts on the molecule if the latter has a permanent magnetic moment whose axis is fixed so that the field exerts a couple on it. If the molecule is magnetically non-isotropic, i.e. if it is not equivalent to a magnetic sphere in its behaviour, the magnetic moment

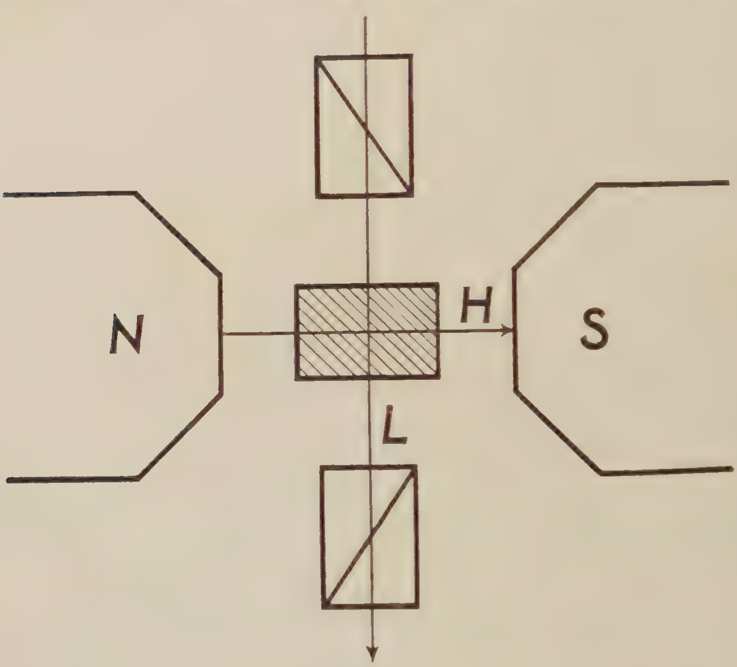

Fig. 1

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* See also C. V. Raman and K. S. Krishnan, *Proc. R. S.* A, **117**, 1 (1927).

has in general a direction inclined to the lines of force and, in consequence, a couple acts on the molecule. In every case the tendency of this couple is to orient the molecule so that the magnetic susceptibility of the system tends to a minimum value. This orientation, however, is unable to exert its full effect.

When dealing with a liquid in which the molecules are in a state of continual thermal agitation we have a kind of statistical equilibrium and the magnetic field tends to orient the molecules. We do not have the molecules oriented at random in all directions but there is a certain preferential orientation of the molecules in that direction in which their potential energy in the field of force is a minimum. This statistical equilibrium can be evaluated, by a well-known method, and if we postulate further that the molecules are not optically isotropic, i.e. that the electrical moments induced in the molecules by the electric field in the light wave are not always parallel to the field, we have as a consequence which, I think, is fairly obvious, that the liquid exhibits a feeble double refraction and acquires some of the characteristics of a crystal. This effect is, however, extraordinarily feeble; in fact, I doubt very much whether, except perhaps in one or two laboratories in the world, the phenomenon has been observed in the course of the ordinary work of the physicist.

I myself have observed it with a small electromagnet and when on one occasion I got the effect in a few minutes I was very jubilant, but in half an hour I discovered that I was observing a small residual Faraday effect, and not magnetic double refraction at all. The position is that the observation is extremely difficult.

Now, obviously, while Langevin's theory gives us a general account of the phenomenon, its real significance is that if we knew the magnetic characteristics and also the optical characteristics of the molecule we could calculate the double refraction and see if this agreed with observation. On the other hand, if we knew the actual magnitude of the double refraction and the optical characteristics of the molecule we could go back and infer from them the magnetic characteristics of the molecule, or at least the degree of magnetic anisotropy of the molecule. That is the importance of double refraction from the standpoint of the theory of magnetism generally.

Perhaps I can make the importance of this clearer by referring to the work of Pascal who some years ago paid a great deal of attention to the examination of the magnetic properties of a great variety of compounds, both organic and inorganic, and attempted to find some general relationship between them. Pascal's work led to the belief that there was nothing startling about diamagnetism and that you could, in general, determine the diamagnetic susceptibility of an organic compound simply by adding up certain contributions from the separate atoms of which the molecule is composed, that is to say, diamagnetic susceptibility is an additive molecular property. In a few cases there were certain residual differences, but later on Pascal made further observations, though I think they are relatively of minor importance from the quantitative point of view. Nevertheless, Pascal emphasised that they constituted an influence of diamagnetism that was not altogether negligible. Pascal's work was concerned largely with liquid or crystalline bodies and in consequence what he was actually measuring was the average susceptibility of molecules oriented in all possible directions relative to the lines of magnetic force. The average susceptibility so measured does not really tell us very much about individual molecules. The results of X-ray work and the fundamental conceptions of chemistry suggest that the molecules are not even approximately isotropic. This being so, if we really wish to understand the architecture of the molecule and determine its magnetic properties we have to study the diamagnetic properties of single molecules, and unless we have such information we cannot really even begin to understand how the problems of structural chemistry are related to the fundamental properties of diamagnetism.

We have, therefore, to seek for some method of investigating the diamagnetic character of molecules. We have dealt hitherto with liquids but when we pass from liquids to crystals we have a complication introduced by the fact that the actual structure of the crystal is not known in many cases; in fact, in most cases it is not known at all. Therefore the work on liquids tends in the direction of simplicity, and it is of importance to try and interpret magnetic double refraction in a quantitative manner and then to deduce the ultimate qualities of the molecules themselves.

This has been the fundamental idea with which we set out. There was, however, a very serious limitation in that the work of Cotton and Mouton was practically confined to certain specified classes of organic compounds, namely the aliphatic compounds, whilst in regard to a great many inorganic compounds they do not, for some reason, appear to have been able to get a measurement or even to observe the effect.

One of the first things we did, therefore, was to try and improve the technique of the subject in such a manner as to bring all known substances within the scope of the research. We felt quite certain that the failure of Cotton and Mouton to observe magnetic double refraction in water or one of the common paraffins was due to the insufficient sensitiveness of their apparatus. Moreover we knew from optical work on the scattering of light that there is no reason to suppose, if a molecule is electrically isotropic, that it must be magnetically isotropic as well. On the other hand, we know that the electrical and magnetic behaviour are counterparts of each other and that there must be correlation between these aspects. Therefore we felt that if the technique of Cotton and Mouton were improved it should be possible to study double refraction in all substances in the liquid state. The problem is twofold. First there must be a sufficiently intense magnetic field, and secondly there must be sufficiently delicate methods of observation. It is obvious that in order to increase the sensitiveness of the method of observation the liquid must be placed in an *intense* magnetic field.

Not possessing the financial resources which seem to lie so close to hand in the case of many American physicists, and perhaps also to some physicists in this country, I wandered about the streets of Calcutta and looked into the old iron shops and discovered a huge dynamo of the Edison type, which had probably figured in some nobleman's house but had been thrown away in favour of some newer model. This dynamo happened to be in perfect order and we got it for the price of the old copper it contained. The old Edison dynamos are enormous and the marked feature of the electromagnet was its great length of 35 cm., while the gap was very small, only about 1 cm.[2] We found that with a current of about 10 amp. we had a field of 25,000 gauss. Using the electromagnet we were able to observe magnetic double refraction in practically all the substances we examined. In order to obtain quantitative results we have had also to develop more sensitive methods of measurement and for this purpose we employed a very interesting device, due to the late Lord Rayleigh*, which proved to be of great service. The set up of the apparatus is given in Fig. 2, which shows diagrammatically the apparatus employed by one of my students, M. Ramanadham†.

S is a "Pointolite" source of light, *L* a converging lens illuminating the slit of the collimator *C*. N_1 and N_2 are respectively the polarising and analysing Nicols. P_1, P_2 are the poles of the electromagnet and *T* the observing telescope. The glass strips *M* and *N* form the compensator. A piece of flint glass, *M*, supported at its ends, is bent in a vertical plane by a small adjustable force applied at its centre. The glass thus strained is interposed between the crossed Nicol prisms. The double refraction induced in the glass plate by the applied stress manifests itself by the restoration of light everywhere in the field of the telescope *T* except along a horizontal dark band corresponding to the neutral axis of the plate *M*. If any doubly refracting medium is interposed between the strained glass and the polariser N_1 a shift of the dark band occurs and can be measured with reference to the cross wire of the observing telescope. In order that both kinds of double refraction may be determined quantitatively this shift is compensated by the interposition of a second glass strip *N* which can be compressed either horizontally (for positive birefringence) or vertically (for negative birefringence). The plate *N* is connected with a pan in which weights can be placed so that the applied stress necessary to compensate the shift can be measured.

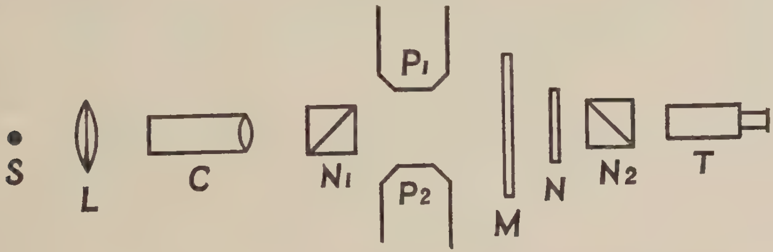

Fig. 2

In this manner Mr Ramanadham has been able to measure the double refraction occurring in a great many common substances, including something like 35 compounds in which Cotton and Mouton failed to observe the effect, and in which it is exceedingly small. There is a large difference between the aliphatic compounds and the aromatic compounds and I have some figures here relating thereto. If we take the double refraction observed with nitrobenzene as 100, the figure for water is only 0·4, and that for ethyl alcohol is of the same order. There is a very remarkable difference referring not only to the magnitude but also to the signs of the double refraction and their relation to chemical constitution. A characteristic feature of the effect as observed by Cotton and Mouton is that all compounds of the benzene series—naphthalene and similar aromatic compounds—show a positive birefringence, whilst the aliphatic compounds show a negative birefringence. In other words, aromatic compounds behave like positive uniaxal crystals, aliphatic compounds like negative uniaxal crystals. The chemist has divided organic compounds into the aliphatic and aromatic classes and the distinction, which is fundamental in chemistry, is reflected magnetically in the fact that one class gives a positive and the other class a negative birefringence. Only, however, by very refined arrangements such as I have outlined is it possible to observe and measure this characteristic difference.

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* *Phil. Mag.* 4, 678 (1902).

† M. Ramanadham, "Magnetic birefringence in liquids," *Indian Journal of Physics*, 4, 15 (1929).

In aliphatic series, the effect of substitution is to produce considerable change in the magnitude of the magnetic double refraction observed. This is shown in the following series of relative experimental values: [nitrobenzene, 100]; formic acid, + 2·5; acetic acid, + 1·1; propionic acid, + 1·1; butyric acid, 0·7; capronic acid, + 0·7; heptylic acid, − 0·5; caprylic acid, 0. We have obtained these results and you will see that formic acid shows a strong positive birefringence. I have no doubt that if we proceed further with the series we have not yet studied some of the higher acids—we shall obtain a negative birefringence. This reversal of the sign of the birefringence is analogous to the reversal of the long chains of fatty acids observed by Müller by X-ray methods. We have shown that a negative birefringence is characteristic of the aliphatic compounds, and the same sort of influence is shown in the ketones and as we proceed up the series we obtain a negative birefringence. On the other hand there is evidence that double compounds have a positive birefringence.

I have given you a few illustrations, but do not run away with the idea that the method is only applicable to organic compounds. It is just as possible to investigate inorganic compounds. In this case, of course, we have only to use solutions of such compounds. Results with some of the nitrates, such as sodium nitrate and nitrites, show that any kind of unsaturation increases the positive birefringence and decrease the negative birefringence. In all this I am merely indicating the field of work that has been opened up by the extending of the work of Cotton and Mouton and the making of their method of investigation applicable to a great variety of substances.

Now I come to the question of the interpretation and use we make of these results. It is not sufficient to say that there occurs positive or a negative birefringence. We must try to deduce the magnetic characteristics and here we are face to face with considerable difficulties. Langevin considered the case of a molecule with an axis of symmetry, and the mathematics becomes much simpler in such a case. We, however, in the general case, have to assume that the magnetic ellipsoid and the optical ellipsoid of the molecule have unequal axes and that these axes may have no obvious relationship to each other. You will find an account of Langevin's theory given in Prof. Born's monograph, *Handbuch der Radiologie*. This theory of Langevin, complicated as it may seem, is inadequate because he has assumed that the polarisation field, i.e. the optical field acting on the molecule, is of an isotropic character.

When we have a beam of light passing through a liquid, the actual electromagnetic field acting on the light wave is due to two causes; one, the external field of the light wave itself, and the other, the optical polarisation of the molecules in the immediate neighbourhood. Langevin and Voigt used the well-known theory of refraction in this matter, but our investigations show that Langevin's theory is quite inadequate, even as an approximation, and when we come to deal with such recondite phenomena as double refraction it is wholely inadequate. Molecules are not spherical in form. They are highly anisotropic. Much depends on how the molecule is oriented in the light wave. Mr Krishnan and myself* have developed a general theory of optical and electrical properties of a liquid and we have been able to show that the influence of the shape of the molecule is, in consequence of its environment, effectually diminished in a manner that can be experimentally determined. The reason I have had to speak about optical anisotropy is that magnetic birefringence depends on *both* optical and magnetic anisotropy.

The value of C_m, the Cotton-Mouton constant†, which is a measure of the optical birefringence exhibited by a liquid in a strong magnetic field is given by the equation

$$\begin{aligned} C_m &= (n_p - n_s)/\lambda H^2 \\ &= -3\,(n_0^2 - 1)^2\,[(A-B)\,(A'-B') + (B-C)\,(B'-C') \\ &\qquad + (C-A)\,(C'-A')]/8\pi n_0 \lambda \kappa T v\,(A+B+C)^2, \end{aligned}$$

where A, B and C are the moments induced by unit electric force in the incident light wave acting along the three mutually perpendicular axes of the optical ellipsoid of the molecule, and A', B', C' are the magnetic moments for unit magnetic fields acting in the same directions. The remaining symbols have their customary significance. It is clear that the sign of C_m depends on that of the factor

$$\Sigma\,(A'-B)\,(A'-B').$$

If the optical moments A, B, C are in descending order of magnitude and if A', B', C' are in the reverse order, then $\Sigma\,(A-B)\,(A'-B')$ is positive and the value of C_m is positive. But if A, B, C and A', B', C' are in the same order, either descending or ascending, then the value of C_m is negative. The quantities A, B, C are connected with the refractive index, n, by the relation

$$(A+B+C)/3 = 3\,(n_0^2 - 1)/4\pi v\,(n_0^2 + 2),$$

so that we have

$$C_m = -\,(n_0^2 - 1)\,(n_0^2 + 2)\,[\Sigma\,(A-B)\,(A'-B')]/60 n_0 \lambda \kappa T\,[\Sigma A].$$

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* *Loc. cit.*

† S. Bhagavantam, *Indian Journal of Physics*, 4, 1 (1929).

If $A = B$, and $A' = B'$, we have

$$C_m = -(n_0^2 - 1)(n_0^2 + 2)(A - C)[3C' - (A' + B' + C')]/60n_0\lambda\kappa T(2A + C)$$

also, if δ be the optical anisotropy, then

$$\delta = (A^2 + B^2 + C^2 - AB - BC - CA)/(A + B + C)^2.$$

It is because the molecule is both optically and magnetically anisotropic that we get double refraction. If we knew the quantities A, B, C and A', B', C' it would be possible to compute the Cotton and Mouton constant absolutely and see if it agrees with observation. I think the principal feature of the theory that Mr Krishnan and I have worked out is the determination of A, B, C and if we could get A', B' and C' we should get a value for the Cotton and Mouton constant. But we do not know A', B' and C'. What we want to do is to know A, B and C and to calculate A', B' and C'. If we assume the molecule to have an axis of symmetry the method becomes a perfectly practicable one. This assumption is definitely permissible in a number of cases. Take carbon bisulphide or benzene. In these cases the assumption of an axis of symmetry is justified and we can go ahead and compute the magnetic characteristics. This was done some time ago* and the remarkable fact was discovered that in the case of benzene the magnetic susceptibility is nearly twice as large in a direction normal to the plane of the ring as in a direction parallel to the ring. In the case of anthracene the magnetic susceptibility in a direction normal to the plane of the benzene ring was four and a half times that in a direction parallel to the ring. This is sufficiently remarkable but I should mention that these compounds show positive and negative birefringence and I come to the simple conclusion that in the case of certain compounds, as for example benzene, maximum diamagnetic susceptibility coincides in direction with minimum optical polarisation-susceptibility. We have here an effect deduced from observation which awaits interpretation, and there is no doubt that it is extremely significant from the point of view of molecular structure.

If I stopped here, as I ought from considerations of time, I should leave the whole subject in an extremely unsatisfactory state. You might very well say that I have discussed double refraction and spoken of light-scattering, but that you know nothing at all about magnetic anisotropy, and yet you are asked to accept the fact of this double refraction, and that this places rather a heavy strain on your credulity.

Fortunately, however, the most interesting things that have come out of our work are conclusions drawn from wholly unrelated fields of investigation. From our studies on light-scattering and other investigations of that kind we can compute the magnetic characteristics of the molecule. This matter is discussed in a paper to be published shortly. If we take, for example, hexamethyl benzene we find that it is a remarkable substance. Lonsdale has analysed its crystal structure, and as soon as we saw his results we came to the conclusion that it should be possible for us, without much difficulty, to determine the magnetic characteristics of this crystal from our investigation of light-scattering, together with our studies of its magnetic birefringence. We proceeded to fix the magnetic axes of the crystal and to find out what should be the magnetic susceptibility normal to the plane of the ring, and also in a direction parallel to it, and the observations showed themselves to be in complete agreement with the results referred to. Hexamethyl benzene, in a direction at right angles to the plane of the benzene ring, behaves as an aromatic compound, whilst in the plane of the ring its behaviour is typically aliphatic and attributable to the CH_3 groups.

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* See e.g. "Magnetic birefringence in liquids of the aliphatic series," by M. Ramanadham, *Indian Journal of Physics*, 4, 15 (1929); and "The anisotropy of the polarisation field in liquids," *ibid.* p. 39.

We appear to have developed a new technique for studying the magnetic characteristics of crystals. This is shown diagrammatically in Fig. 3. The apparatus is based essentially upon the gravity balance of Threlfall and Pollock* and was used by S. Bhagavantam†. A fine quartz fibre is stretched across the poles of the electromagnet *NS* as shown and is kept taut by two screws. A glass fibre carrying the crystal, *C*, between the poles of the electromagnet is attached to the quartz fibre as shown, so that the crystal hangs in the non-homogeneous field of the electromagnet. As the quartz fibre is stretched across the gradient parallel to the field, it at once responds to forces acting on the crystal in the direction of this gradient and the resultant twist of the quartz fibre results in an angular displacement of the end of the glass fibre which is measured by a microscope.

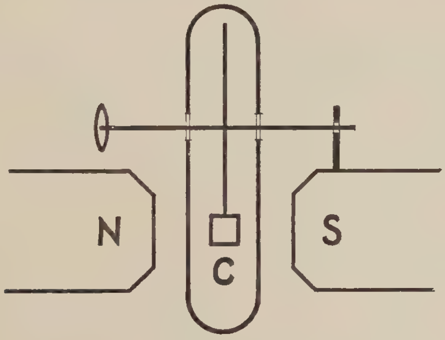

Fig. 3

I have taken up a large amount of time and I cannot describe to you in any detail all the various kinds of instruments we have developed for our investigations. This new technique, however, has been applied to a very large number of organic crystals, so that we now have a means for direct quantitative observation of the magnetic characteristics of organic crystals, especially naphthalene, anthracene, hexamethyl benzene and a number of others. I want you to realise that here we have the beginning of a practically limitless field of research. The organic chemist manufactures and the physicist designs for our benefit thousands and thousands of crystals, all of which await a detailed study of their magnetic construction. This field of work might perhaps at one time have been considered too unimportant because the effects exhibited were so small, but I hope you will realise from what

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* *Phil. Trans.* A, **193**, 215 (1899).

† *Loc. cit.*

I have been telling you that the magnetic anisotropy of an organic crystal is a remarkable phenomenon, the diamagnetic susceptibility being four or five times greater in one direction than in another. Important results must consequently follow from an extended study of the diamagnetic behaviour of organic crystals. I would be failing in my duty if I did not emphasise to you that this new technique enables us to go much farther than has been possible by older methods in the matter of crystal structure. X-ray analysis is a most powerful method of research and I would be the last to decry it because I use it myself, but there are limitations to the X-ray method, and the magnetic study of crystals has revealed properties which are at present beyond the reach of X-ray examination. I will take as an illustration the case of hexamethyl benzene. One would assume that it has axes of symmetry and that the magnetic susceptibility is the same in all directions and that likewise the optical susceptibility is the same in all directions. In one respect, as stated already, this substance is an aromatic compound but in another it is aliphatic in character, a peculiar combination. There is a difference of about 10 per cent. in the magnetic susceptibility along the two axes of the plane of the ring and these two axes coincide absolutely with the optical axes in that plane. Here we have, therefore, the optical and the magnetic susceptibilities following each other closely. That is what we should expect from the crystal structure. I cannot understand at present chemically why it should be asymmetrical, but it *is* asymmetrical.

I will not stop here but will trespass further on your patience and indicate a still further possibility of this work. Take that very interesting and remarkable substance azobenzene, which is the starting-point of a great industry, viz. the manufacture of dyes. Azobenzene is composed of two benzene rings bridged together by an azo group. This substance has been examined and it has been found that the crystal does not show that high degree of magnetic anisotropy which we should have expected from the existence of two benzene rings presumably in the same plane; at least this is the structure the chemists provide us with. There must be something in the crystal structure which masks the magnetic anisotropy; in other words, there must be more than one molecule in the lattice and these molecules must be so oriented relatively to each other that in the crystal itself there occurs a masking of the anticipated magnetic anisotropy. One can predict that the two molecules in the crystal lattice cannot be oriented parallel to each other. Similarly, I fear that in the case of naphthalene and benzene, the orientation which Sir William Bragg, in his book published some years ago, assigned as probable, cannot now be accepted, because it does not take into account the optical and magnetic aspects and there is evidence that more recent X-ray results will lead to a revision of their structures so as to fit in with the optical and magnetic characteristics. Optical and magnetic characteristics never mislead X-ray results may sometimes mislead.

You see now that starting from the molecule we have entered into the crystal region and provided we have enough data in these two fields of research, magnetic study can be regarded as a most powerful auxiliary to crystal analysis. That is the point I am trying to make.

I should like to mention another very remarkable new field of research in elation to diamagnetism which we have entered upon. For a long time it has been art of our scheme of research on magnetism in Calcutta to investigate how the hysical state of a substance influences the magnetic characteristics. Suggestion ave been made that the diamagnetism of certain compounds is different in the iquid state from what it is in the solid state. Mr V. I. Vaidyanathan* started a research ome time ago in Calcutta to develop a complete technique by which the feeble iamagnetism of vapours and gases could be accurately measured. The method is n extremely simple one; it was first used by Faraday and was modified by Glaser nd by Hammar.

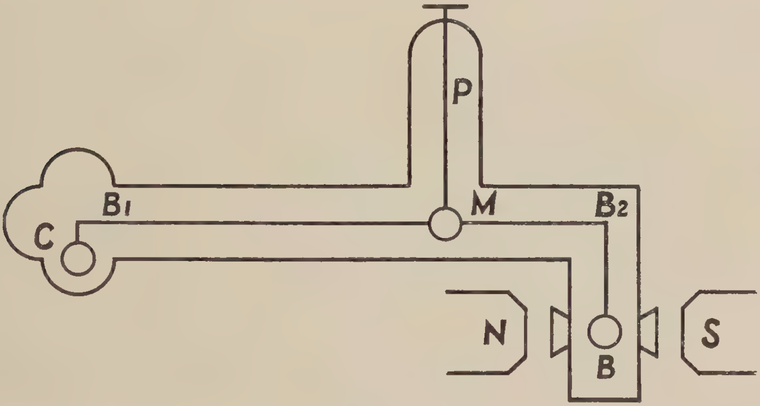

Fig. 4

A thin aluminium vane $B_1 B_2$, Fig. 4, carrying a concave mirror, M, is suspended y a phosphor bronze strip within a vessel of the form shown, which can be filled ith any gas or vapour. One end of the vane carries the evacuated glass bulb, B, hilst the other end carries a counterpoising bulb C. B is suspended in the agnetic field of the electromagnet NS.

The glass of the bulb B is specially chosen so as to have the smallest possible agnetic susceptibility. It is highly paramagnetic, so that magnetically this glass ulb is practically neutral. By suspending it inside the cylinder containing the gas r vapour—a magnetic analogue of the principle of Archimedes—we can determine he magnetic susceptibility of the gas or vapour. One of the firstfruits of the ethod which we devised was connected with results obtained by Glaser, who nvestigated CO_2 and one or two other inorganic gases and came to the conclusion hat the susceptibility of a gas is not proportional to the pressure. Glaser laid it own that at low pressures, instead of the magnetic susceptibility decreasing roportionally to the pressure, the susceptibility pressure curve departed from this inear relationship. That result caused a great deal of sensation and got into the ext-books, which ought not to have happened. As a matter of fact, I saw this paper f Glaser's on a Saturday afternoon and on the following Tuesday evening I gave n Address, proving to my own satisfaction, if not to the satisfaction of my audience, hat Glaser's work must be wrong and his result attributable to faulty technique.

* *Indian Journal of Physics*, **1**, 183 (1926).

Glaser explains the result as due to some orientation of the molecules in the magnetic field. If such an orientation exists, we know from our work on double refraction that the effect of orientation is exceedingly small. The Cotton and Mouton constant contains the factor 10^{-14}, so that you will realise at once what an exceedingly small effect it is. In view of that, Glaser's statement that the molecules are orientated is palpably wrong. The subsequent work of Glaser I believe to be fallacious, but that was the starting-point, and one object which led us to develop this new technique of placing the vacuum bulb in a heterogeneous magnetic field was the investigation of his conclusion*. We have found throughout strict proportionality between pressure and the value of susceptibility for carbon dioxide, argon, hydrogen, and all gases examined, and are convinced that Glaser's conclusion is erroneous.

I wish to say, however, that this field of work must be extended largely. We have tried to extend it and there are two or three cases of very great interest in which the physical state does seem to produce a most remarkable change in diamagnetism. The most remarkable cases are those of graphite, charcoal and diamond. Pascal worked with many organic compounds and also with the above forms of carbon. Values of the diamagnetic susceptibilities (in 10^{-6} units) found by Pascal are: graphite, $-4{\cdot}0$; charcoal and diamond, $-0{\cdot}5$. In other words, magnetically diamond and charcoal are alike. Why is it that graphite has a higher value? Graphite stands out alone of all forms of carbon as having a diamagnetic susceptibility about eight times as high as the others. That suggests that there must be something peculiar about graphite and we set to work and carried out some experiments. We have found that the susceptibility of massive graphite is still higher; the average value is something like $-7{\cdot}0 \times 10^{-6}$. Graphite is magnetically anisotropic, the diamagnetic susceptibility normal to the plane of its structural ring (in 10^{-6} units) being -18, whilst in the plane of the ring the value is -2. We find with graphite that the value can be brought down to the value for sugar charcoal by powdering of the graphite; in other words, particle size determines the magnetic susceptibility of graphite. But the powdering must be extremely fine to achieve the result. The same sort of thing is found in the case of bismuth and antimony, and we now know that particle size has an influence on the diamagnetic property and there is obviously a relationship between the fact that the susceptibility is greater in the direction normal to the plane of the ring†.

I have tried to give you some idea of the kind of work that is being attempted in Calcutta. We have only just started these investigations and they have to be pursued and developed. We have obtained some results but we are yet far from being able to picture them and explain them in terms of the newer theories. Nevertheless, I think that what I have said will indicate that there is still plenty of room for experimental work in modern physics.

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[*] Glaser, *Ann. der Physik*, **74**, 459 (1924); Hammar, *Proc. N. A. S.* **12**, 594 (1926); Vaidyanathan, *Indian Journal of Physics*, **1**, 183 (1926), **2**, 135 (1928).

[†] See S. Paramasivan, "Anomalous diamagnetism of graphite," *Indian Journal of Physics*, **4**, 141 (1929).

SOME NOTES ON WIRELESS METHODS OF INVESTIGATING THE ELECTRICAL STRUCTURE OF THE UPPER ATMOSPHERE (II)

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ABSTRACT. The comparative discussion of the various direct wireless methods of measuring the "equivalent" height of the atmospheric ionized region, begun in the first part of this paper, is continued so as to include the recently described moving-transmitter method of Mirick and Hentschel.

The relations between the optical and equivalent paths of waves deviated by the upper atmosphere and between the rates at which these quantities may vary with time are investigated theoretically, and, from the results of experiments carried out to test these relations, deductions are made concerning (*a*) the existence of more than one ionized region in the upper atmosphere, (*b*) the possible influence of magnetic storms on atmospheric ionization, (*c*) the gradient of ionization in the upper atmosphere and its alteration under solar influence at sunrise, and (*d*) the actual height reached by waves deviated in the upper atmosphere.

§ 1. INTRODUCTION

In a previous paper* of similar title a comparison was made of the various direct wireless methods that are now available for measuring the "effective height" of the atmospheric ionized layer and it was there shown that, for a layer of horizontal stratification and for conditions under which the earth's magnetic field may be neglected, the same quantity, namely the equivalent path of the atmospheric waves, was measured by all methods. The effective height of the layer, which may be deduced from the equivalent atmospheric wave path thus found, was shown to be greater than the actual maximum height reached by the waves in the process of atmospheric deviation.

The present paper continues in three directions the discussion begun in part I. In the first place it brings up to date the general enquiry into the significance to be attached to the term "effective height" of the ionized layer, by the inclusion of a discussion of a new wireless method of height determination recently described by Mirick and Hentschel†. Secondly, it presents a discussion of the relations which exist between the equivalent and optical paths of the atmospheric waves and the theoretical significance of the variations of these quantities with time and with the frequency of the sending station. The discussion of experimental data which then follows consists in part of an enquiry as to how far the theoretical conclusions of this and the previous paper fit in with the experimental results, and in part of deductions which can be made from the data as to the actual electrical structure of the upper atmosphere.

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* *Proc. Phys. Soc.* **41**, 43 (1928). For convenience this paper will throughout be referred to as "part I."

† *Proc. Inst. Rad. Eng.* **17**, 1034 (1929).

§ 2. THE MOVING-TRANSMITTER METHOD OF HEIGHT DETERMINATION

In the course of observations made on the intensity of signals emitted by an aeroplane in flight, Mirick and Hentschel, of the United States Naval Research Laboratory, noticed periodic variations of signal strength at a rate which remained fairly constant over a considerable time interval; and, by assuming that such signal variations were due to interference between direct waves and indirect waves which had been reflected by the upper atmosphere, they were able to deduce from their observations the effective height of the Kennelly-Heaviside layer. For the purpose of their calculation Mirick and Hentschel examined the imaginary case of a fixed emitting source and a moving observer, the latter travelling towards or away from the sender so as to pass through the maxima and minima of the interference system formed by the direct and indirect trains of waves. They then assumed that the same results would apply if the relative velocity between the source and the observer were due to the motion of the source, the observer being at rest. From the rather involved formula resulting from such a calculation it is not easy to see exactly what significance should be attached to the term "effective height" in this case, and the following alternative way of regarding the problem is therefore offered.

Let us consider the aeroplane sending station as travelling towards the observer with a velocity v. If the frequency of the waves emitted by this station when at rest is f_0 the frequency of the waves travelling towards the observer will, by Doppler's principle, be f_1, where

$$f_1/f_0 = c/(c - v) \qquad \text{......(1)},$$

c being the velocity of electric waves in free space. Let us now suppose that the atmospheric waves which ultimately reach the observer set out from the sender in a direction making an angle θ_0 with the vertical. The frequency of these waves will therefore be f_2, where

$$f_2/f_0 = c/(c - v \sin \theta_0) \qquad \text{......(2)}.$$

If now we have $c \gg v$, as is actually the case in practice, (1) and (2) may respectively be written

$$f_1/f_0 = (c + v)/c \qquad \text{......(1}\,a\text{)},$$

and

$$f_2/f_0 = (c + v \sin \theta_0)/c \qquad \text{......(2}\,a\text{)},$$

so that

$$(f_1 - f_2)/f_0 = v\,(1 - \sin \theta_0)/c \qquad \text{......(3)}.$$

Now the uniform succession of signal maxima and minima experienced at the receiver may be regarded as beats of frequency $(f_1 - f_2)$ produced by the direct and indirect waves. As this quantity* is measured directly, sin θ_0 may be estimated if the velocity of the aeroplane is known.

It is therefore evident that in the moving-transmitter method, for an ionized layer of horizontal stratification, the angle of incidence at the layer is measured. The height deduced from this quantity is therefore the same as that obtained by means of the other methods previously discussed. This quantity, which has been termed the "equivalent height," is greater than the actual maximum height reached by the atmospheric waves.

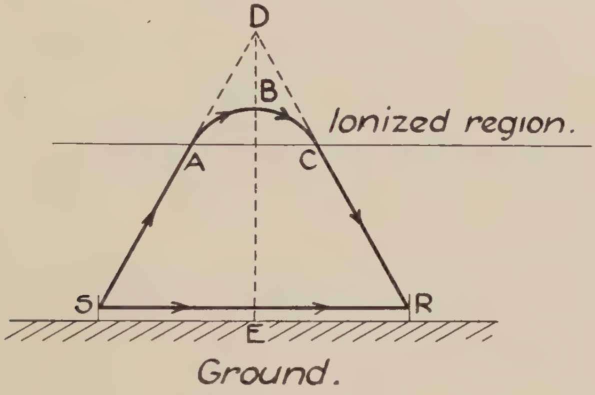

Fig. 1. Diagram of ray track.

Combining the above result with those arrived at in part I, we may summarise as follows:

(1) The frequency-change† method and the group-retardation method measure the same quantity, namely $c \int \frac{ds}{U}$ for the atmospheric waves, where ds is an element of the atmospheric wave track along which the group velocity is U.

(2) The angle-of-incidence method and the moving-transmitter method both enable us to find the angle of incidence of the atmospheric waves at the lower boundary of the layer.

(3) For cases in which the influence of the earth's magnetic field is negligible (e.g. for short waves) all four methods enable us to deduce the equivalent path

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[*] The magnitude of $(f_1 - f_2)$, in the cases dealt with by Mirick and Hentschel, ranged from 0·1 to 0·4 cycles per second.

[†] In part I this was termed the wave-length-change method, but, in view of the present day tendency in wireless terminology, the name frequency-change method seems preferable. In the application of this method the interference phenomena which are observed are produced artificially by continuous variation of the frequency of an unmodulated continuous wave through a small range. A modification of this method may, however, be noted as specially suitable for ultra-short wave working, in which the modulation frequency of a telephony station and not the carrier frequency is varied continuously through a small range. Experiments have already been carried out with this method and it is hoped to give an account of the modifications it entails in a future paper.

OLD SYNDICATE ROOM

$\int \frac{ds}{\mu}$ of the atmospheric waves (μ being the refractive index at any point along the path) which is equal to $SD - DR$ in Fig. 1; from a knowledge of this the equivalent height DE may be calculated.

§ 3. THE RELATION BETWEEN OPTICAL PATH, EQUIVALENT PATH AND FREQUENCY

In part I a distinction was drawn between the optical path $\int \mu ds$ and the equivalent path $c \int \frac{ds}{U}$ of the atmospheric waves. For short waves we may write $U = c\mu$ so that the equivalent path becomes $\int \frac{ds}{\mu}$. Since, in the ionized medium, μ is less than unity the equivalent path is greater than the lineal trajectory of the wave track, while the optical path is less. The equivalent path may be measured directly while the optical path can only be deduced indirectly and approximately after an interpolation. As will be shown below, it is however possible to measure directly the rate of change of optical path with respect to time, although the actual magnitude of the optical path may not be known. We shall call the optical path P and the equivalent path P'. Both P and P' are functions of the frequency and, as shown in part I, are related as in (4).

$$P' = P + f.dP/df \qquad \text{......(4)},$$

where f is the mean frequency of the waves, so that

$$P = \frac{1}{f}\int_0^f P'df \qquad \text{......(5)}.$$

To estimate the value of P a curve exhibiting the relation between P' and f must be drawn. By extrapolation from this curve to zero frequency the value of the integral in (5) may be estimated for any particular frequency and the optical path thus found for that frequency.

When both the equivalent path and the optical path of the atmospheric waves are known for any particular frequency a rough estimate may be made of the geometrical length of the path. This is most easily seen in the case of vertical incidence, for in that case the actual height $s/2$ reached by the waves must lie between $P'/2$ and $P/2$.

The results immediately above are independent of the particular law of dispersion which is valid for the propagation of waves in the ionized medium, so long as the group velocity is less and the phase velocity greater than the velocity of light in free space. It is therefore evident that the relation between P' and f, which may be determined experimentally, is of the greatest importance.

If the law of dispersion for the layer is that usually taken as the basis of the theory of ionic refraction when the earth's magnetic influence is neglected, we have

$$\mu^2 = 1 - Ne^2/\pi m f^2 \qquad \text{......(6)},$$

where N is the number of electrons, of charge e and mass m, per c.c. at any point. In such a case it is possible to proceed much further in the interpretation of the (f, P') curve, in that the actual height reached by any particular frequency and also the gradient of ionization in the layer may then be deduced.

Before proceeding to the general case of any type of ionization gradient it is instructive to consider first the two special types of gradient discussed in part I.

We take first the case in which the ionization N varies directly as the height y above a certain level h. We then have, from (6),

$$\mu^2 = 1 - ay/f^2 \qquad \text{......(7)},$$

where a is a constant. In such a case the equivalent path of the atmospheric waves* is given by

$$P' = 2h/\cos\theta_0 + 4f^2\cos\theta_0/a \qquad \text{......(8)},$$

where θ_0 is the angle of incidence of the waves at the layer. For vertical incidence this becomes

$$P' = 2h + 4f^2/a \qquad \text{......(9)},$$

so that this type of gradient would be indicated by a parabolic (f, P') curve, from which h and a could be determined. For this particular case the geometrical length of path s of the atmospheric waves may be shown to be equal to $2h + 2f^2/a$, so that the actual height reached by waves of frequency f would be half this quantity.

For the second type of gradient, in which the ionization is taken as varying as the square of the height y above the lower boundary of the layer, supposed to be situated at a height h, we have†, corresponding to (7), (8) and (9), the following equations:

$$\mu^2 = 1 - by^2/f^2 \qquad \text{......(10)},$$

where b is a constant, $$P' = 2h/\cos\theta_0 + \pi f/b^{\frac{1}{2}} \qquad \text{......(11)},$$

and, for vertical incidence, $$P' = 2h + \pi f/b^{\frac{1}{2}} \qquad \text{......(12)}.$$

In this case therefore the relation between P' and f is linear, and from it h and b may be deduced. The actual length of path s of the atmospheric waves may be shown to be $2h + 2f/b^{\frac{1}{2}}$, so that the height reached by any particular frequency is half this value.

In either of the two cases considered above, since the actual height reached by any particular frequency f may be found and since at that height we know that the value of the electronic density N is equal to $\pi m f^2/e^2$, μ in (6) being zero‡, it is evidently possible to deduce the relation between ionization and height.

I am greatly indebted to Dr W. de Groot of the Physical Laboratory of Philips Lampworks, Holland, who, in the discussion of a lecture at Eindhoven, pointed out to me that the general problem of the determination of the actual height reached by waves of any frequency from the relation between equivalent height and frequency is entirely analogous to a dynamical problem solved by Abel many years ago, the equation to be solved being, in fact, that known as Abel's integral equation*. The general analogy between these dynamical and wave-problems is being fully dealt with by Dr de Groot elsewhere and only the solution of the integral equation so far as it concerns the problems discussed immediately above need be given here. Let us write (6) as

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* Part I, p. 51 (28) and (30).

† Part I, p. 51 (29) and (31).

‡ This statement requires further qualification. Strictly the value of μ never beomes zero, for such a condition requires that there shall be no absorption, and absorption is never absent. However, as μ tends to zero, the wave-length in the medium tends to infinity, so that reflection proper occurs.

$$\mu^2 = 1 - Ne^2/\pi m f^2 = 1 - N'/f^2 \qquad \text{......(13).}$$

In the case, say, of vertical incidence, we have

$$P' = \int \frac{ds}{\mu} = 2h + 2\int_0^{y_0} \frac{dy}{(1 - N'/f^2)^{\frac{1}{2}}} \qquad \text{......(14),}$$

where y_0 is the height at which $N' = f^2$. The value of $2h$ is that of P' when f is zero, and must obviously be found by extrapolation from the (f, P') curve. Eq. (14) may be written

$$\frac{P' - 2h}{2f} = \frac{\phi(f)}{2f} = \int_0^{y_0} \frac{dy}{(f^2 - N')^{\frac{1}{2}}} \qquad \text{......(15).}$$

Our problem is therefore to find y in terms of N', $y = \psi(N')$, say, when $\phi(f)$ is known. The solution of (15) is†

$$\psi(N') - \psi(0) = \frac{1}{\pi}\int_0^{N'^{\frac{1}{2}}} \frac{\phi(f)}{(N' - f^2)^{\frac{1}{2}}} . df \qquad \text{......(16),}$$

so that if y_0 is the actual height above h reached by waves of frequency f_0 we have

$$y_0 = \frac{1}{\pi}\int_0^{f_0} \frac{\phi(f)}{(f_0^2 - f^2)^{\frac{1}{2}}} df \qquad \text{......(17).}$$

If therefore the heights to which different frequencies penetrate are known, the ionization as a function of the height may be deduced.

§ 4. THE RELATION BETWEEN THE TEMPORAL RATES OF CHANGE OF THE OPTICAL AND EQUIVALENT PATHS

As was mentioned in the last section, the optical path of the atmospheric waves cannot be measured directly, though its approximate value may be deduced from the relation between equivalent path and frequency. It has been shown recently‡, however, that it is possible to measure the rate at which the optical path is changing with time, even though the magnitude of the optical path itself is not known. To do this the numbers of interference fringes produced by (*a*) increase and (*b*) decrease of the transmitter frequency through a known range in a known time are compared.

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* Abel, *Œuvres*, *Journ.* **1**, 11. See also Tait, *Proc. R. S. E.* 1874–5; and Bateman, *Brit. Ass. Report* 1910, p. 352.

† See Tait and Steele, *Dynamics of a Particle* (London, 1878), p. 406, where the following problem is proposed and solved. "To find the curve in which the time of descent to the lowest point is a given function $\phi(a)$ of a, the vertical height fallen through."

‡ *Proc. R. S.* A, **126**, 548 (1930).

Let us suppose that the optical path difference is altering at a definite rate dP/dt, t being the time. Then we can regard the frequency of the atmospheric waves as being $\frac{f}{c} \cdot \frac{dP}{dt}$ cycles per second less than that of the ground wave, so that beats will be produced. Let us now suppose that at the same time the frequency of emission is steadily increased. So far as this effect alone is concerned the down-coming waves will be $\frac{P' - P_0'}{c} \cdot \frac{df}{dt}$ cycles per second lower in frequency than the ground waves, P_0' being the equivalent path of the ground waves. The number of beats per second dn_1/dt between ground and atmospheric waves due to these two effects combined will therefore be given by

$$\frac{dn_1}{dt} = \frac{P' - P_0'}{c} \frac{df}{dt} + \frac{f}{c} \frac{dP}{dt} \qquad \text{......(18).}$$

If now the frequency of emission is steadily decreased, the rate of change of optical path remaining as before, the number dn_2/dt of beats per second produced by the two effects is now given by

$$-\frac{dn_2}{dt} = -\frac{P' - P_0'}{c} \frac{df}{dt} + \frac{f}{c} \frac{dP}{dt} \qquad \text{......(19).}$$

In practice we actually find the numbers Δn_1 and Δn_2 of signal maxima produced by first an increase and then a decrease in the transmitter frequency continuously through a range Δf in a time Δt, so that from (18) and (19) we have

$$P' - P_0' = c\left(\frac{\Delta n_1 + \Delta n_2}{2\Delta f}\right) \qquad \text{......(20),}$$

and

$$\frac{dP}{dt} = \frac{c}{f}\left(\frac{\Delta n_1 - \Delta n_2}{2\Delta t}\right) = \lambda\left(\frac{\Delta n_1 - \Delta n_2}{2\Delta t}\right) \qquad \text{......(21),}$$

where λ is the mean wave-length. The equivalent path P' and the rate of change of the optical path dP/dt may therefore be derived from these measurements since P_0' is known, and, if the observations are repeated at intervals, the rate of change of the equivalent path with time may also be found, so that dP/dt and dP'/dt may be compared.

The results of part I may be used to show the relations that may exist between dP/dt and dP'/dt in special cases. We take first again the case of ionization varying as the height above a certain height h. For vertical incidence we then have, as before,

$$P' = 2h + 4f^2/a \qquad \text{......(9),}$$

and also*

$$P = 2h + 4f^2/3a \qquad \text{......(22).}$$

Now the optical path may vary owing to an alteration of h or to an alteration of a. The first would be an alteration of the height of the layer as a whole, while the second would be an alteration due to some readjustment of the ionization N*.

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* See part I, p. 51 (30).

Evidently in the first case we should have dP'/dt equal to dP/dt, while in the second case dP'/dt would be equal to $3 . dP/dt$*.

For the second case previously considered, in which the ionization varies as the square of the height above the lower boundary of the layer at height h, we have, for vertical incidence,

$$P' = 2h + \pi f/b^{\frac{1}{2}} \qquad \text{......(12),}$$

and also†

$$P = 2h + \pi f/2b^{\frac{1}{2}} \qquad \text{......(23).}$$

In this case therefore an alteration of the height of the layer as a whole would again be shown by the equality of dP'/dt and dP/dt, while for an alteration of the ionization within the layer dP'/dt would be equal to $2 . dP/dt$.

I am much indebted to my colleague Prof. A. E. Jolliffe for friendly assistance with the general case of ionization varying as the nth power of the height y above the lower boundary of the layer at height h. The value of the refractive index μ is now given by

$$\mu^2 = 1 - Ay^n \qquad \text{......(24),}$$

where A is a constant. In this case, for vertical incidence we have

$$P^1 = \int \frac{ds}{\mu} = 2h + 2\int_0^{A^{-1/n}} \frac{dy}{(1 - Ay^n)^{\frac{1}{2}}} = 2h + \frac{2}{A^{1/n}} \cdot \frac{\Gamma\left(\frac{1}{n} - 1\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{1}{n} - \frac{1}{2}\right)} \qquad \text{......(25),}$$

and

$$P = \int \mu ds = 2h + 2\int_0^{A^{-1/n}} (1 - Ay^n)^{\frac{1}{2}}\, dy = 2h + \frac{2}{A^{1/n}} \cdot \frac{\Gamma\left(\frac{1}{n} + 1\right)\Gamma\left(\frac{3}{2}\right)}{\Gamma\left(\frac{1}{n} + \frac{3}{2}\right)} \qquad \text{......(26).}$$

An alteration in the height of the layer as a whole would mean an alteration in h and would be shown by equal alterations in P and P'. On the other hand a re-adjustment of ionization in the layer would mean an alteration in the value of A, for which case

$$\frac{dP'}{dP} = \frac{dP'}{dt}\bigg/\frac{dP}{dt} = \frac{n+2}{n} \qquad \text{......(27),}$$

a general formula which includes the two examples discussed above as special cases.

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* This significance of the relation between optical and equivalent paths has been recently discussed by G. Breit, *Proc. Inst. Rad. Eng.* 17, 1815 (1929), who has also suggested means by which the group-retardation method can be modified so as to measure the phase of the downcoming waves.

† See part I, p. 51 (31).

§ 5. EXPERIMENTAL RESULTS AND DISCUSSION

Measurements of equivalent height by different methods. As has been shown above, we should expect the values of the equivalent height obtained by the frequency-change method and the group-retardation method to be the same if the observations are made under the same experimental conditions. So far no exact comparison has been made by use of the same wave-length, but a comparison on slightly different wave-lengths is possible. For example, Hafstead and Tuve* in America, using the group-retardation method and 70-metre waves, found heights of 252, 235, 225, 232, 225, 232, 220, 225, 226 and 232 km. (average 231 km.) on different days between October 19 and November 17, 1928. These results may be compared with those of a recent series of measurements made with the frequency-change method and 100-metre waves, in which equivalent heights of 223, 229, 224, 235, 245, 223, 250 and 223 km. (average 231 km.) were recorded. The observations in the latter series were made on consecutive days from December 10 to December 17, 1929, at the Radio Research Station, Slough, on transmissions from the National Physical Laboratory. The agreement between the results obtained by the two methods is therefore very good. It should be added that, in the English series of observations, there were also indications of partial reflection from a height of about 105 km. on four of the eight days in question, supporting the conclusion previously arrived at that there are two regions in the upper atmosphere which reflect wireless waves. Further reference is made to this matter below.

In the case of the comparison of results obtained by the angle-of-incidence method with those obtained by either the frequency-change or the group-retardation method, it is important to remember that unless very short waves are used, and unless the layer is horizontally stratified, we must not necessarily expect agreement. Unfortunately, no data for such a comparison of equivalent-height measurements with short waves are available, but a comparison can be made for medium wave-lengths. In Fig. 2 are shown the results of a series of observations made at Peterborough on transmissions from Birmingham on June 30, 1927, in which the equivalent height of the layer was measured simultaneously by both the angle of incidence method and the frequency-change method. These observations were made immediately after sunrise, when conditions are specially favourable for such a comparison, since during that period a single down-coming wave, free from secondary waves, is usually received.

It will be seen that, although the average heights by the two methods are about the same, the departure from the average is much greater in the case of the observations made by the angle of incidence method than in the case of those made by the frequency-change method. This difference can perhaps be explained by the assumption that "reflection" does not always take place at a point mid-way between the two stations, in which case we infer that the layer cannot always be regarded as horizontally stratified and that the stratification varies with time.

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* *Proc. Inst. Rad. Eng.* **17**, 1521 (1929).

The existence of more than one ionized region in the upper atmosphere. The first set of observations on the diurnal variation of the equivalent height of the Kennelly-Heaviside layer were made with 400-metre waves, for which it was usually found that, after sunset, the equivalent height increased slowly, reached a maximum before sunrise, and subsequently fell rapidly to the daytime value. On certain occasions, however, during the few hours before dawn, penetration of the layer was found to take place, the waves then being reflected by an upper region which was richer in ionization. For convenience, the Kennelly-Heaviside layer or lower region has been termed *E* region, while the upper region has been termed *F* region.

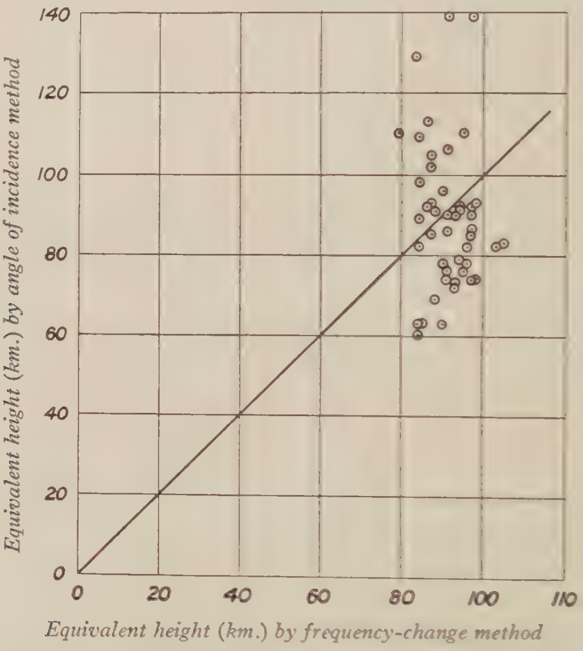

Fig. 2. Birmingham transmission received at Peterborough, June 30, 1927. Wave-length 491 metres.

With 100-metre waves it has been found that penetration of the lower region *E* takes place on all nights, reflection taking place from the upper region *F*. On the majority of days the same result is found during the daylight hours, but, on some days, the ionization in region *E* is sufficient to bring about the reflection of waves of this length. During the daytime, therefore, with 100-metre waves, one of two ranges of equivalent heights, corresponding to the two regions, may be recorded. On occasion it is found that reflection from both regions takes place simultaneously, and the heights of both regions may be measured. At other times it is found that, in a series of observations made at five or ten minute intervals, region *E* and region *F* (or *vice versa*) are recorded in successive observations indicating a rapid decrease (or increase) in the ionization of region *E*. Photographic records illustrating this are given below. A typical series of observations in this connection is that made at King's College, London, on January 13, 1929, with 99·8-metre waves from the Teddington transmitter, when the following equivalent heights in kilometres were measured at 10 minute intervals between 10.0 a.m. and 2.0 p.m. G.M.T.: 229, 229, 236, 244, 217, 229, 229, 230, 204, 196, 229, 100, 99, 93, 98, 99, 96, 98, 232, 99 (and 220), 99, 229, 229, 99. It will be seen that these heights fall into two definite series of mean values, 226 km. and 98 km.

Another phenomenon, which illustrates the physical significance to be attached to the term "equivalent path," may also be noted. It is sometimes found that, even within such a short interval as a minute, quite definite variations of equivalent height are observed, which, if interpreted as variations in the position of the layer as a whole, would indicate extremely rapid movements. There is, however, another possible explanation in terms of the variations of the ionization density of the region through which the waves have to pass before reaching the region where they are reflected. This is suggested by the fact that during the daytime, when conditions are otherwise normally very stable, a sudden increase in the height of region *F* is accompanied by partial reflection from region *E*, while, on the other hand, a sudden fall in the height of region *F* is accompanied by the disappearance of reflected waves from region *E*. As examples of these effects the following results may be quoted; they all refer to transmissions on 100-metre waves from Teddington, the receiving stations being at King's College, London, and at the Radio Research Station, Slough.

(*a*) On December 3, 1929, the average height of region *F* recorded at King's College was 230 km., while that recorded at Slough was 238 km. (The difference is considered as being outside the limits of experimental error.) At the same time there were noted signs of reflection from region *E* at Slough throughout the series of observations, but no such signs were observed at King's College. The occurrence of reflection by region *E* therefore seemed to be accompanied by a greater equivalent height of region *F*.

(*b*) On December 4, 1929, at Slough, reflection from both regions took place at 12.5 p.m. and 12.10 p.m., heights of 243 and 112 km. being measured. At 12.15 p.m., however, all signs of reflection from region *E* had disappeared, and a height of 227 km. was recorded. At the same time there was noted a large increase in the amplitude of the downcoming waves from region *F*.

(*c*) At 12.25 p.m. on December 19, 1929, at Slough, rapid variations of the equivalent height of region *F* took place within one minute. At the same time the amplitude of the downcoming waves from region *F* was found to vary, an increase of equivalent height being accompanied by a reduction in amplitude and also by the development of signs of reflection from the lower region. Within this minute the equivalent height was found to increase from 230 km. to 240 km., the amplitude at the same time being reduced to about 40 per cent. of its original value.

The above results leave little doubt that the rapid variations in the equivalent height of region *F* measured during the day are not due to motions of region *F* at all, but to the influence of the ionization in the lower region *E*. An increase in ionization brings about a reduction in the refractive index μ and so increases the equivalent path $\int \frac{ds}{\mu}$ for waves which pass through this region. At the same time the absorption of waves passing through it is increased.

In observations made during a magnetic storm, Hafstead and Tuve* recorded that the height of the ionized layer was abnormally great, and Maris and Hulbert† have interpreted this as an increase in the actual height of the reflecting region. It is clear from what has been said above that though this may have been the case it was not necessarily so, for an increase in the ionization in the lower regions of the atmosphere due to the magnetic storm would reduce the group velocity of the waves in those regions and thus give a fictitious increase in the height of the region that actually reflected the waves. In this connection it is of interest to note that the reflection of 70-metre waves from the abnormally great equivalent heights of region F, observed by Hafstead and Tuve during the magnetic storm of October 18, 1928, was accompanied by reflection from region E at a height of 100 km., although reflection from this lower region was not observed on the days either preceding or succeeding the magnetic storm.

The temporal rates of change of optical and equivalent paths. As has been shown above, it is possible to measure the rate of change of the optical path of the atmospheric waves by comparing the numbers of signal interference maxima produced by increasing and decreasing frequency-changes made at the sending station; and further, from a comparison of the rates of change of the equivalent and optical paths, it is possible to derive information relating to the type of variation in ionization which is responsible for these changes. Experiments designed to measure dP'/dt and dP/dt for this purpose were begun on April 26, 1929, with 100-metre waves from the Teddington transmitter, which were received at King's College, London, and at the Radio Research Station, Peterborough. Previous observations had shown that the equivalent height of the F region fell rapidly in the early morning, and this period was therefore considered a suitable one for measuring also the rate of change of optical path.

A typical series of the results obtained is shown in Fig. 3, where the values of the equivalent path of the atmospheric waves and the rate of change of optical path at different times on April 26, 1929, are shown. The two curves exhibit an interesting correlation. When the equivalent path is increasing, the optical path is seen to be increasing, while when the equivalent path is decreasing, the optical path is seen to be decreasing also. At about 4.44 a.m. the rate of decrease of the equivalent path is a maximum, while about this time the rate of change of optical path is also a maximum. During this period of rapid change the rate of change of equivalent path is definitely greater than the rate of change of optical path, the ratio being about 1·3. To get a more accurate comparison, a 20 minute continuous series of observations was made between 4.50 a.m. and 5.10 a.m., both P' and dP/dt being measured every minute. These results provide a very accurate comparison, and how that the average value of dP'/dt was 2·9 km./min., while that of dP/dt during he same period was 2·3 km./min.

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* *Terr. Mag. and Atmos. Elect.* **34**, March (1929).

† *Proc. Inst. Rad. Eng.* **17**, 494 (1929).

During the period from 6.00 a.m. to 6.30 a.m. it is noted that the rate of ecrease of optical path was actually greater than the rate of decrease of equivalent ath; this indicates a state of affairs quite different from that obtaining earlier.

Special interest is attached to the period when the equivalent height is falling apidly owing to the renewal of solar influence at sunrise. In the example quoted bove, the ratio of dP'/dt to dP/dt was 1·3. For the same morning period on anuary 17, January 31 and February 11, 1930, this ratio was also found to be greater than unity, the respective values being 1·9, 1·9 and 2·2. We therefore conclude that the reduction in equivalent height which takes place in the early morning cannot be brought about solely by a reduction in the height of the layer as a whole but must be either wholly or partly brought about by an increase of onization within the layer.

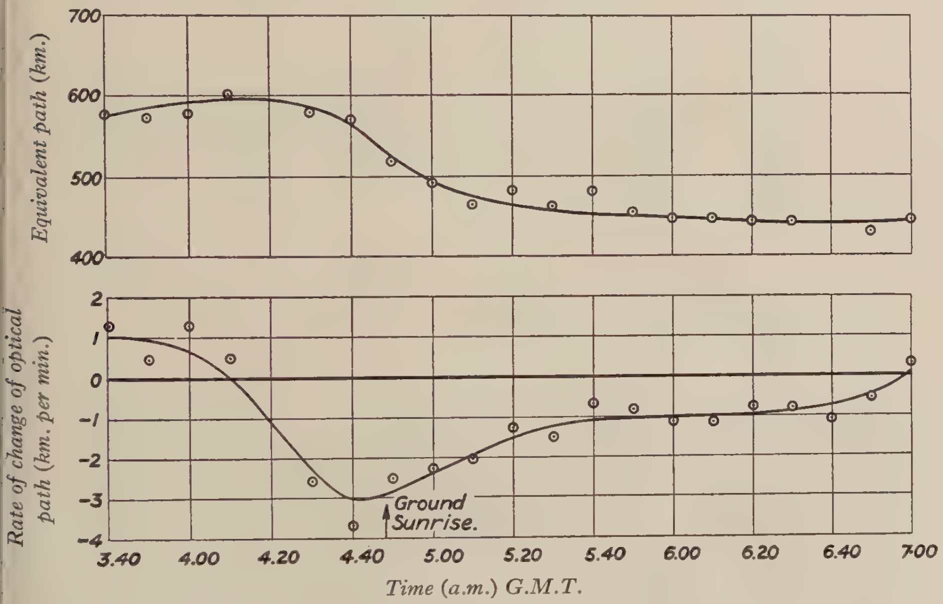

Fig. 3. Teddington transmission received at King's College, London, April 25, 1929. Wave-length 100 metres.

For the morning period succeeding the period of rapid fall, when the equivalent path seems practically constant while the optical path is steadily decreasing, another influence seems to be at work. During this period it is known that region E is forming in gradually increasing density. This formation would produce a gradually decreasing optical path and an increasing equivalent path for rays passing through this region. It appears possible, therefore, for a fall of the actual height at which waves are reflected in region F to be compensated, so far as equivalent-path measurements are concerned, by an increase in ionization in region E, so that practically no variation in equivalent height results.

Similar results were found for the early morning period when a wave-length of 150 metres was used. In Fig. 4 is shown the variation of the equivalent path with time on March 21, 1930, for this wave-length. The transmission took place from the National Physical Laboratory and was received at King's College, London. It is seen that up till 6.30 a.m. the atmospheric waves were deviated by region F, but that after about this time region E formed in sufficient intensity to reflect. During the period of the rapid reduction in the equivalent height of region F measurements of dP/dt were made also, so that dP'/dt and dP/dt could be compared. The values of these quantities are given in the table:

Table: Corresponding values of dP'/dt and dP/dt

Time	dP'/dt (km. per min.)	dP/dt (km. per min.)	dP'/dP
5.20 a.m.	− 20	− 4·7	4·25
5.30 a.m.	− 7·5	− 3·35	2·2
5.40 to 6.0 a.m.	− 2·35	− 2·6	0·92
6.10 to 6.30 a.m.	+ 0·6	− 2·5	− 0·24

These results may be explained in exactly the same way as those obtained when a wave-length of 100 metres was used. The fact that dP'/dP is greater than unity during the period of rapid reduction of equivalent height clearly excludes again the possibility of the layer's falling as a whole, and we must regard the reduction in the optical and equivalent paths as being due chiefly to alterations in the ionization gradient. The fact that the value of dP'/dP gradually fell from about 4 to 2 during the same period indicates that the value of n in (27) and in the expression for μ, viz. $(1 - Ay^n)^{\frac{1}{2}}$, increased from about $\frac{2}{3}$ to 2, so that the effect of solar radiation was to sharpen the boundary between the non-refracting and refracting regions.

For the period immediately succeeding that of rapid fall the equivalent and optical paths were altering in opposite senses. This is what we might expect as a result of the formation of region E. The reduction in the refractive index of that region, due to gradually increasing ionization, would increase the equivalent path and reduce the optical path for waves which pass through it.

It may not be superfluous to add that when both P' and P are decreasing, the actual length of paths of the downcoming waves is being steadily reduced at a rate which lies between dP'/dt and dP/dt. This follows because ds/dt must lie between the limits of $\frac{d}{dt}\int\frac{ds}{\mu}$ and $\frac{d}{dt}\int\mu . ds$.

During the daytime, variations in the optical path of the downcoming waves are not usually marked. On one occasion, however, on December 3, 1929, between 12.15 and 12.30 p.m., a slow increase of optical path of downcoming rays from egion F (indicated by the number of "fringes" for increasing frequency changes eing slightly larger than those for decreasing frequency changes) took place hroughout the period of the test. At the same time the equivalent height was found o decrease slightly. These changes may be interpreted as indicating the steady eduction in the ionization of region E, which would increase the value of P but lecrease the value of P' for the waves passing through it.

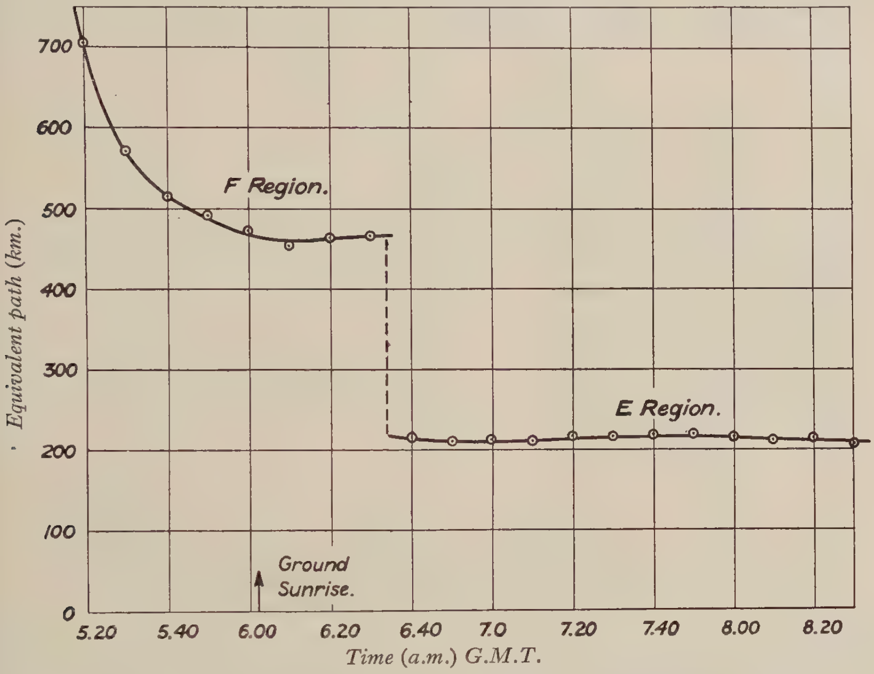

Fig. 4. Teddington transmission received at King's College, March 21, 1930.

The variation of equivalent path with frequency. It has been shown in § 3 that information relating to the actual height reached by the atmospheric waves may be derived from the curve exhibiting the relation between P' and f. It will be easily understood, however, that the experimental difficulties of getting the necessary simultaneous measurements of P' for different values of f, in order to construct such a curve, are very great and, as yet, no such complete series of observations is available. We can, however, get a rough idea of the shape of this curve if we take the average of the results obtained on different days. In that case it is, of course, important to include only observations made at the same time of the day and only those obtained when reflection for all the frequencies used is taking place from the same region (i.e. say from region E). The time chosen in this connection is the period consisting of the two hours after ground sunrise when the equivalent heights measured do not as a rule vary rapidly with time.

The average values of P' for different frequencies corresponding to wave-lengths of 400, 212, 150, 130 and 100 metres for observations at short distances (i.e. at

King's College, London, and at Ditton Park on transmissions from Teddington) are exhibited in Fig. 5. The observations are perhaps not accurate enough in this connection to enable us to be quite certain whether the curve is linear or parabolic for the higher frequencies and thus enable us to decide between ionization gradients varying with the square of the height or with the height above the lower boundary of the layer, and more data are being sought in this connection.

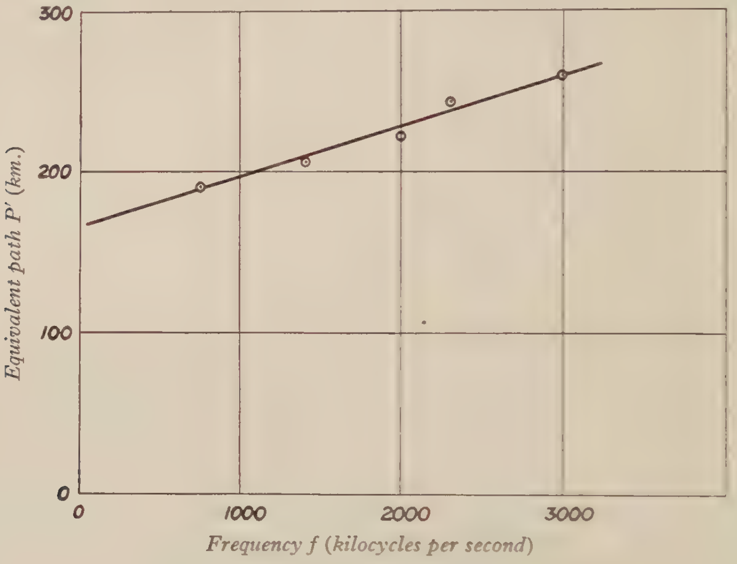

Fig. 5. Average values of P' for short distances.

The curve, however, does enable us to determine without very grave error the optical path P for the highest frequency used (i.e. 3000 kc. sec.), for the exact nature of the extrapolation to zero frequency cannot affect the value of the integral required to any large extent. The value of P for 100-metre waves is in this way found to be 212 km., and since the case in question is one of approximately vertical incidence we know that the actual height reached by the atmospheric waves lies between 106 km. and 129 km. The results of § 4 and equations (28) and (29) in Part I show that the actual height lies nearer $P/2$ than $P'/2$ and it may be shown that this quantity would be 112 km. for an ionization gradient varying linearly with the height, and also about the same value for an ionization varying as the square of the height above the lower boundary of the layer. The (f, P') curve also shows that ionization begins to be appreciable at this time of the day at a height of about 80 km. since this is the value of $P'/2$ when f is zero.

Although a complete set of observations for any one morning is not available, the results of many early morning measurements leave little doubt that there is a discontinuity in the experimental (f, P') curve, so that its form for a wide range of values of f must be roughly somewhat as indicated in Fig. 6.

The critical value of f for which the penetration of region E just takes place lepends on the time of the day at which observations are made, the value just efore dawn sometimes corresponding to a wave-length of 400 metres, while the alue during the daytime corresponds to a wave-length of about 100 metres. The uestion whether, from this diagram, we can derive information relating to the ctual height reached by waves reflected by region F by the method adopted for egion E therefore arises. In this connection let us first consider the variation of ptical path with frequency. If, for a particular frequency f_1, the waves just enetrate the lower region there will be a discontinuity in the relation between P and f at this frequency so that the equivalent path P', which is equal to $P + f\frac{dP}{df}$, will be infinite for the same frequency. In trying to find P for a frequency such as f_2 in Fig. 6, we must therefore recognise the fact that, in integrating the area between the (f, P') curve and the f axis, the value of P' is infinite* at $f = f_1$. This result seems to indicate that we cannot rigorously obtain the integral required, so that the actual height reached by waves which are deviated by the upper region cannot be obtained by the method in question.

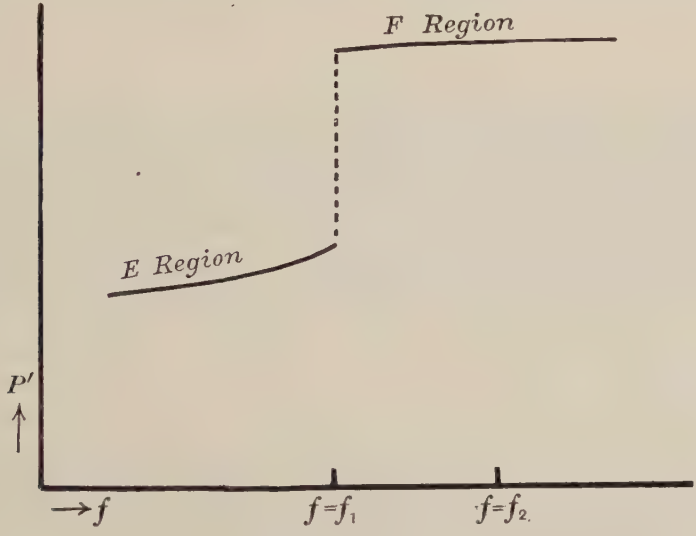

Fig. 6. General form of P'/f curve.

Some typical photographic records. On plate I, (*a*) to (*d*), are reproduced some illustrative records obtained by the frequency-change method. In all cases they represent the variation of signal intensity with time. During the periods when the frequency is changing (which are usually from two to three seconds in duration) interference maxima and minima are artificially produced. The signal variations

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[*] The fact that for a critical frequency the equivalent path is theoretically infinite and therefore the group velocity zero may perhaps be of importance in connection with the explanation of echoes of long retardation.

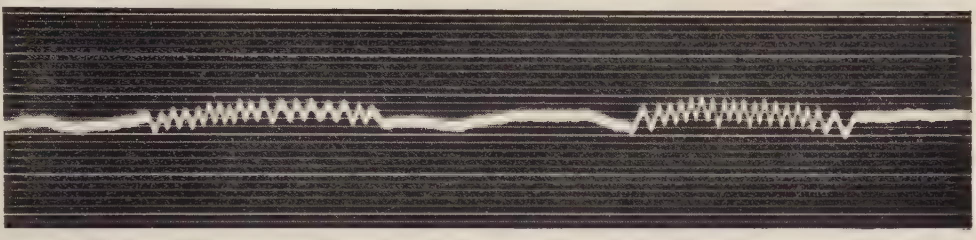
during the intervals when the frequency of the sending station is maintained constant are due to natural variations in the intensity and phase of the downcoming waves. In all cases the number of signal maxima (Δn) divided by the frequency change (Δf) which produced them gives the difference in the times required for a group of waves to travel from sender to receiver via the atmosphere and via the ground, so that $c.\Delta n/\Delta f$ is the equivalent path difference. When the optical path is altering it is important to note that the mean of the two values of Δn for increasing and decreasing frequency changes must be used in this connection (see § 4). In all cases, except where the contrary is stated, the emitting station was at Teddington and the receiving station at Ditton Park.

Records (a) and (b) illustrate the sudden change from reflection at region F to reflection at region E; (a) was made at 12.5 p.m. on November 26, 1929 and (b) ten minutes later. The sudden reduction in Δn from 18·0 to 9·5 means that the equivalent path of the atmospheric waves was almost halved. The frequency change for both records was 10·4 kc. sec. and the mean frequency 3000 kc. sec. (wave-length 100 metres). In record (b), since the value of Δn is greater for decreasing than increasing frequency-changes, the optical path of the downcoming waves must have been decreasing slowly.

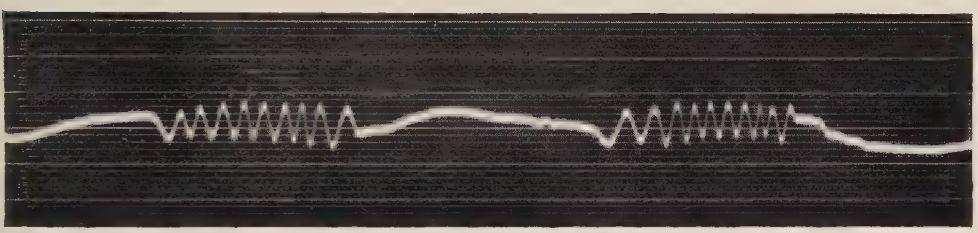
Record (c) illustrates what has been termed "phase-fading." It was made at 7.40 a.m. on January 31, 1930, with a wave-length of 150 metres, and shows the optical path of the downcoming waves, reflected by region F, to be steadily decreasing. This is indicated by the fact that the value of Δn is greater for decreasing than for increasing frequency-changes. At the beginning of the record, when the emitted frequency was constant, the steady reduction in optical path produced slow regular beats of period about 3·7 sec., indicating that the optical path of the downcoming waves was being reduced by 150 metres in that time. This corresponds to a value of – 2·4 km./min. for dP/dt. The same quantity can be found from the difference in Δn for increasing and decreasing frequency changes. For example, for substitution in (21), we have $\Delta n_1 = 22{\cdot}5$, $\Delta n_2 = 23{\cdot}8$, $\Delta t = 2{\cdot}5$ sec., so that dP/dt is – 2·4 km./min.

Record (d) was made at King's College at 7.11 a.m. on February 14, 1930, the mean wave-length being 150 metres. It illustrates the gradual growth of subsidiary "fringes" during the short period of $2\frac{1}{2}$ sec. in which the frequency change took place. Since the subsidiary maxima are just more than twice as frequent as the primary maxima, equivalent paths in the ratio of just over 2 to 1 are indicated, the subsidiary maxima being most probably due to waves which had been twice reflected by the ionized region.

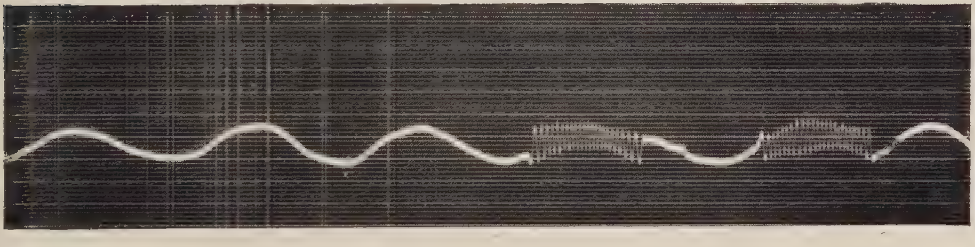
(*a*)


Time
Frequency increasing
Frequency decreasing

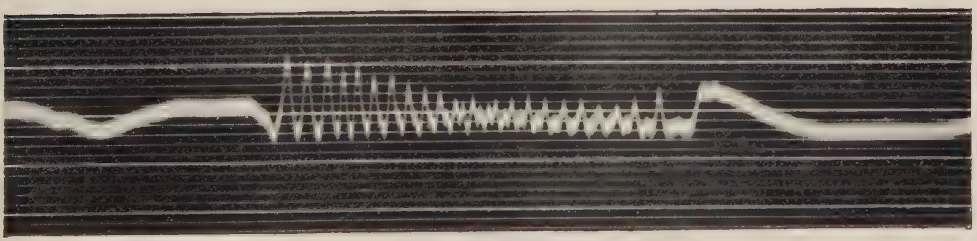
(*b*)


Time
Frequency increasing
Frequency decreasing

(*c*)


Time
Frequency increasing
Frequency decreasing

(*d*)


Time
Frequency changing

§ 6. ACKNOWLEDGMENTS

In conclusion I wish to express my indebtedness to Mr E. L. Hatcher and Mr A. C. Haxton who have carried out the transmissions from the National Physical Laboratory on which the majority of the observations recorded above were made, and also to Mr W. C. Brown and Mr R. D. Gander for valuable technical assistance at the Ditton Park and King's College, London, receiving stations respectively. I also wish to thank Mr A. L. Green, M.Sc., for assistance in the reduction of some of the data. Finally I wish to acknowledge the kind collaboration of Dr D. W. Dye, F.R.S., who has made accurate measurements of the frequencies and frequency-changes used throughout the series of experiments described above.

The problems discussed arose in connection with work carried out for the Radio Research Board of the Department of Scientific and Industrial Research.

INTERFERENCE MEASUREMENTS WITH SINGLE MOLECULES

Lecture delivered on April* 11, 1930, *by*

PROF. P. DEBYE, the Physical Institute, University of Leipzig.

In the elementary classical theory of the diffraction of X-rays by crystals every atom is supposed to be the centre of a secondary radiation. The observed effects are accounted for by the phase-differences of the secondary rays set up by the spacial arrangement of the atoms in regular lattices. Now the regularity of the atomic arrangement and the large number of atoms involved, although responsible for the special character of the crystal-scattering, are by no means essential for the creation of an interference effect itself. Any atomic structure will give rise to interferences; and even if only a very small number of atoms be contained in such a structure an effect should still be observable, provided only that the wave-length of the radiation is comparable with the atomic distances. The difference between this type of interference effect and the effect of a crystal grating should not be larger than the difference, say, between the scattering of light by an ordinary grating and the scattering of it by a few parallel slits. We cannot but believe that the chemical formulae in common use are a geometrical representation of the real spacial arrangement of the atom in the molecule. For this reason we have to expect that even for a single molecule, containing perhaps only a few atoms, the angular intensity-distribution of, say, scattered X-radiation will show the effect of the path-differences arising from the peculiar spacial distances between the atoms in the molecule. The observation of such an effect must therefore lead to the absolute measurement of atomic distances in free molecules.

In practice, however, it is not possible to observe the scattering from one single molecule. The best one can do with X-rays, for instance, is to observe the energy scattered by something like 10^{16} molecules at a time, corresponding to the amount of matter contained in 1 mm.^{3} of a gas at atmospheric pressure. Here, then, a serious difficulty seems to arise. Though all these molecules have the same constitution, each of them will give a different angular distribution of scattered intensity, for this distribution will be essentially dependent on the orientation of the molecule with respect to the primary ray. So it is not impossible that if one molecule gives a maximum of intensity in a certain direction, another molecule will give a minimum of scattered intensity in the same direction, merely because it has another orientation. In these circumstances it might be suspected that the summation of all the primary molecular effects, as it is performed in an actual experiment, would destroy everything observable. Fortunately, however, this is not the case. A simple calculation shows that the interference effect cannot be entirely obliterated, even by the most irregular distribution in orientation*. A well-known illustration of an effect of the same kind is given by the powder-method in X-ray crystal-analysis†.

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* Mr L. Woodward, of Oxford, who is working in the Leipzig Laboratory, has had the kindness to correct this account.

To express this result in a formula let us consider a molecule containing atoms 1 ... i ... n, each of these atoms being characterized by a scattering function ψ_i. Then taking the average over all possible orientations, the scattered intensity J will be proportional to the expression

$$J = \frac{1 + \cos^2\theta}{2} \sum_1^n \sum_1^n \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}} \qquad \text{......(1).}$$

In this formula the summation is to be taken twice over all the atoms and

$$x_{ij} = ksl_{ij} \qquad \text{......(1'),}$$

where l_{ij} is the distance of any atom i from any other atom j, $k = 2\pi/\lambda$ (λ denoting the wave-length of the primary radiation), and $s = 2 \sin \theta/2$ (θ denoting the angle between the primary and the secondary ray). The factor $(1 + \cos^2\theta)/2$ has been introduced to allow for the effect of the polarization accompanying the scattering. The function $\sin x/x$ shows maxima and minima (decreasing in magnitude with increasing order) and so also the whole sum expressing J will in general not give a function which decreases steadily with increasing angle θ. As one of the simplest applications we may consider the case of the CCl_4 molecule, neglecting for the moment the scattering of the central carbon atom, because of the relatively small number of electrons it contains. According to van't Hoff and Lebel the chlorine atoms are arranged at the corners of a regular tetrahedron. The distance of a Cl atom from any other Cl atom therefore is the same, say l, and we only have one value of x, namely

$$x = ksl.$$

Also there exists only one function ψ, the scattering function of the Cl atom. The intensity function is thus

$$J = \frac{1 + \cos^2\theta}{2} 4\psi^2 \left[1 + 3\frac{\sin x}{x}\right] \qquad \text{......(2).}$$

Let us for the moment make the assumption (which we shall justify later) that the influence of the scattering function ψ is only of secondary importance. Let us further consider the intensity curve corrected for the polarization-effect, that is to say not J itself but $2J/(1 + \cos^2\theta)$. Then we have to expect that the scattering of CCl_4 vapour will show maxima and minima in its angular distribution corresponding to the maxima and minima of the function $\sin x/x$. The first maximum should occur (with very good approximation) for $x = 5\pi/2$ and as $x = ksl = 4\pi (l/\lambda) \sin(\theta/2)$, we have to expect the first maximum for an angle θ defined by the equation

$$\sin\frac{\theta}{2} = \frac{5}{8}\frac{\lambda}{l} \qquad \text{......(3).}$$

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* P. Debye, *Ann. der Phys.* **46**, 809 (1915); P. Ehrenfest, *Amsterdammer Akademie*, **23**, 1132 (1915).

† P. Debye and P. Scherrer, *Göttinger Nachr.*, Dez. 1915; *Phys. Zeitschr.* **17**, 277 (1916); A. W. Hull, *Phys. Rev.* **10**, 661 (1917).

With a given wave-length of the primary radiation, it will only be necessary to observe this maximum and the angle θ for which it occurs to be able to calculate the distance l of the Cl atoms in the single free molecule.

It might appear feasible to observe the scattered radiation from liquids, instead of using gases as is supposed in the foregoing considerations. In liquids the molecules are also oriented at random and the scattered intensity is much larger. Moreover, a great number of liquids have already been investigated and at least one interference maximum has been observed in every case. A closer examination of the condition in liquids, however, shows that here we are not dealing with a pure case of intermolecular interference. There is no reason why this effect should not exist in liquids, but it is certain that at the same time another intermolecular effect is superposed due to the interference of the secondary rays emitted by different molecules. It is this last effect which is responsible for the main part of the interference picture as it is ordinarily observed. No theory exists which is perfect enough to eliminate from the observed intensity-curve the part due to intermolecular interference. So we are left with the necessity of eliminating this effect experimentally and this is done by the use of matter in the gaseous state. Here on the average the molecules are far enough apart to diminish the intermolecular interference effect to such a small fraction of the total effect, that it can be completely disregarded. By this remark I do not mean to say that the observation of the X-ray scattering by liquids is not in itself interesting enough. But by such experiments we do not learn so much about the intra-atomic structure of the molecules; it is the peculiar average regularity in the distribution of the whole molecules with respect to each other which gives the clue for the explanation of the greater part of the interference pattern. Even so it must be emphasized that a satisfactory discussion of the interference phenomena for liquids can only be based on a knowledge of the scattering function of the single molecule. Therefore in this field also the experiment with the gas should come first.

The first experiment was carried out with CCl_4 vapour*. A narrow primary X-ray beam of circular cross-section was passed through a layer of the vapour a few mm. thick at a temperature of approximately 20° above the boiling point and at atmospheric pressure. The primary rays were emitted by a copper-target and consisted for the larger part of the K radiation of this metal (wave-length 1,539 A.U.). The bottom of the box containing the vapour consisted partly of a sheet of aluminium 0·01 mm. thick. A few cm. from this box a photographic plate was mounted to register the secondary radiation emitted by the vapour, whereas the primary ray was absorbed before it could strike the plate. As the result of a twenty hours' exposure a ring was photographed encircling the centre corresponding to the primary ray. So it was proved that in the scattered radiation of the CCl_4 molecule a maximum of intensity occurs at least in one direction making an angle of approximately 36° with the primary ray.

This apparatus, however, was not very suitable for the observation of the scattered intensity over a larger range of angles. Moreover, it seemed possible to diminish the time of exposure appreciably by another design, especially of the cross-section of the primary bundle. So the following experiments* were carried out with another apparatus, the principle of which is made clear by Fig. 1. The primary ray now has a rectangular cross-section of 1 × 4 mm.^{2}; it passes again through a metal box containing the vapour, which is heated electrically. Ordinarily it is absorbed at the end of its path through the vapour. By removal of a slide at the end for a short time it can be allowed to pass through in order to print a mark on the film characterizing the direction of the primary ray ($\theta = 0$). Just beneath the primary beam and as near as possible to it is a window 6 mm. by 3 mm., covered with aluminium foil of thickness 0·01 mm. Through this window the scattered radiation of the vapour leaves the box and is photographed on a film enclosed in a circular film-holder which is centred on the window. The front part of this film-holder consists of black paper and the back part has double walls, between which water is kept running to cool the film, which might otherwise become too hot owing to the heat coming from the gas-box. The details of the inner construction of the box and of the part defining the primary beam were carefully designed to prevent secondary or tertiary radiation of the walls from passing through the window. This last condition in particular made it necessary to use different apparatus for different parts of the angular range. Three modifications of the apparatus are in use; with the one appropriate for small angles the smallest angle obtainable is $\theta = 8°$.

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* P. Debye, L. Bewilogua and F. Ehrhardt, *Phys. Zeit.* **30**, 84 (1929).

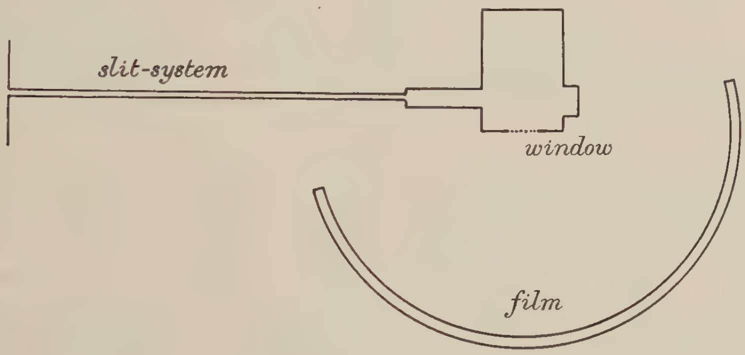

Fig. 1.

With the new equipment it was possible to observe in the case of CCl_4 vapour and with copper K_α-radiation the first three interference-maxima. They occur approximately at the angles $\theta = 36°$, $\theta = 65°$, $\theta = 110°$. The time of exposure was reduced to about 4 hours. By application of equation (3) the distance l between the Cl atoms can easily be calculated from the angle of the first maximum. The result is $l = 3{\cdot}1$ A.U.

In deriving this equation I had to point out that it can only hold to a first approximation, namely so far as the influence of the atomic scattering function can be neglected. In fact in the discussion leading to equation (3) I treated the atomic scattering function ψ merely as a constant. Now from the experiments on the scattering of X-rays by crystals we already know that ψ is by no means a constant, but that the intensity scattered by an atom decreases markedly with increasing angle θ. From the point of view of the theory we can explain this behaviour again by the interference principle. In fact the dimensions of the electronic atmosphere constituting the atom are comparable with the wave-length of the X-radiation. Therefore at not too small an angle θ the scattered rays coming from different parts of the atom will have path-differences of appreciable magnitude and can destroy each other by interference. If we had a picture of the electronic density in the atom as a function, say, of the distance from the nucleus, we should at once be able to calculate how ψ will vary with the angle θ.

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* P. Debye, L. Bewilogua and F. Ehrhardt, *Sächs. Akad. Ber.* **81**, 29 (1929).

The whole calculation* and its result become very simple if we assume that the electronic density around the nucleus is a function of the distance r proportional to the probability-function e^{-r^2/a^2}, a being a constant characterizing the "mean radius" of the electronic density distribution. If then the atom contains z electrons, ψ will be the proportional to the expression

$$ze^{-k^2a^2s^2/4}.$$

As $s = 2 \sin (\theta/2)$ this calculation shows that the scattered amplitude will decrease with increasing angle and this decrease will be the steeper the larger the "mean radius" of the atom. To show the influence of this behaviour of ψ on the scattering curve for the molecule the scattered intensity has been plotted in Fig. 2 as a function of x, where $x = ksl$, for a diatomic molecule consisting of two atoms at a distance l. The different curves correspond to different values of a; in the upper curve a has been taken as equal 0. To illustrate the effect of the assumption about the molecule in the different curves, every curve is accompanied by a picture of the molecule in which circles are drawn at a distance $r = 2a$ from the nuclei. The distance l of the atomic centres is always the same. From the picture of Fig. 2 we see that the finite dimensions of the atoms will have a double influence.

Firstly with increasing atomic dimension the decrease of the total intensity becomes more and more pronounced. As soon as the atoms become large enough to be approximately equal to half the distance between them the maxima and minima generated by the interference between the radiation of the two atoms will disappear. The experimental evidence supports this conclusion. From scattering experiments with O_2 and N_2 of the same kind as those described for CCl_4 no maximum can be detected; if, however, two Cl atoms are connected with one C atom, as in CH_2Cl_2, the intermolecular interference effect can readily be detected. Another example is furnished by the molecules CO_2 and CS_2. Whereas in the former case the interference maxima are only faintly indicated, they are very pronounced in the latter.

Secondly, there is another influence of the atomic size which is of importance even if the effect of the atomic scattering function is not large enough to destroy the intermolecular interference maxima altogether. The upper curves in Fig. 2

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* P. Debye, *Phys. Zeitschr.* **31**, 419 (1930).

show how with increasing atomic size the first minimum is shifted to the right, whereas the first maximum is shifted to the left. In the application of equation (3) to the calculation of the atomic distances no allowance has been made for this shift and therefore the value of l calculated in this way needs correction.

Although the foregoing discussion is good enough to show the result of the atomic size in a general way, it is not sufficient as a basis for a calculation of the correction. This is due to the fact that the assumed distribution-function for the electronic density in the atom represents the real distribution only very incompletely. Now Thomas* and Fermi† have shown independently how to arrive at a fairly good approximation of the electron distribution in the atom. Applying essentially the same principle of calculation which had already proved of value for the discussion of the distribution of ions in a liquid and thereby for the properties of strong electrolytes, they arrive at a density function for the atom. The application of their result to our case is especially simple because of the fact that in the approximation attained by the Thomas-Fermi method the density-distribution curve for any atom can be simply read off from one single universal curve by mere adjustment of the scale for the distance r according to the number of electrons contained in the atom considered. From this property of the distribution curve it follows that the

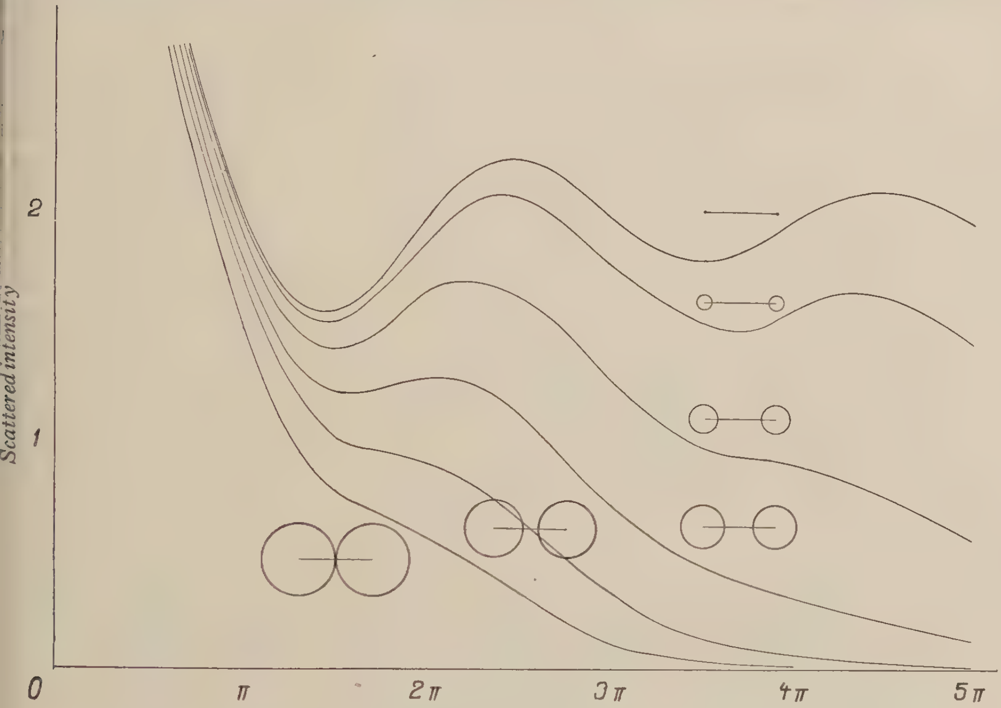

Fig. 2. Scattering curves for various values of a (see p. 344).

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* L. H. Thomas, *Proc. Cambr. Phil. Soc.* **23**, 542 (1927).

† E. Fermi, *Zeit. für Phys.* **48**, 73 (1928).

scattering function ψ of any atom can also be read off from one universal curve, in this case by adjustment of the scale of the variable s, or $2 \sin (\theta\ 2)$ according to the particular atom considered and the wave-length used. The universal curve itself cannot be expressed by a simple function and had to be calculated numerically*.

Taking account of this correction the intensity scattered by the CCl_4 molecule, corrected for the polarization, has been calculated and is plotted in the lower curve of Fig. 3. The upper curve represents the intensity when the atomic size is neglected. The abscissae are x/π. On the other hand, the films obtained in the CCl_4 experiments were recorded with a Zeiss recording photometer. The ordinates of the recorded curves were reduced to intensity values by the help of intensity marks obtained by the photographing of the primary radiation through a rotating sector. In this way it was possible to draw an experimental intensity curve for the scattering of the CCl_4 molecule. This curve is shown in Fig. 4 *b*, the abscissa being s, where $s = 2 \sin (\theta/2)$. The angle θ itself has also been indicated to show that the observation of the scattering for large angles near 180° is not important. The experimental curve is to be compared with the theoretical curve, already plotted as the lower curve in Fig. 3. To make the comparison easier this curve has been plotted a second time in Fig. 4 *a* with enlarged ordinates of the approximate size of the ordinates of the experimental curve, Fig. 4 *b*.

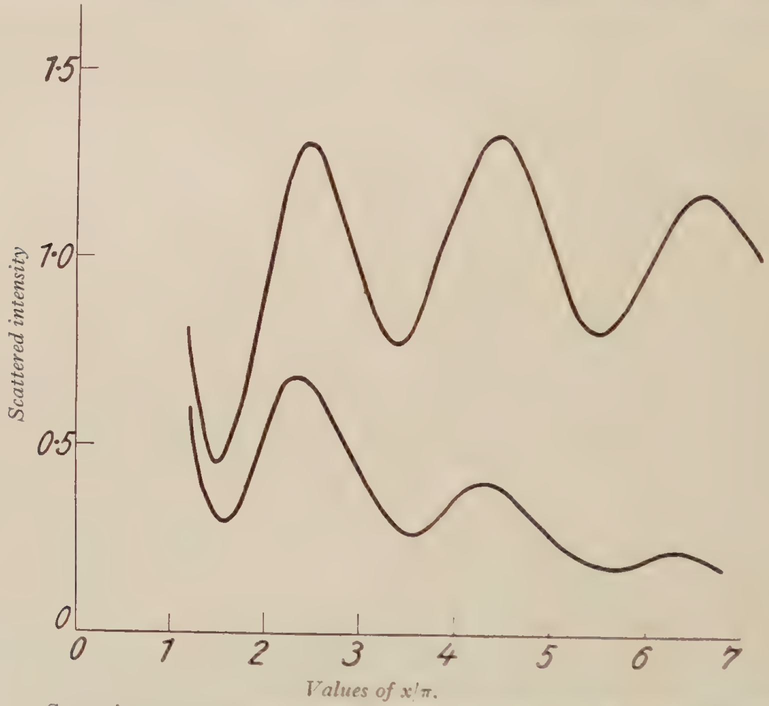

Fig. 3. Scattering curves calculated for $C\,Cl_4$ molecule, with and without correction for atomic size.

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* The calculation in *Phys. Zeit.* **31**, 419 (1930) checks with the formerly published values of W. L. Bragg and S. West, *Zeit. für Krist.* **69**, 118 (1929).

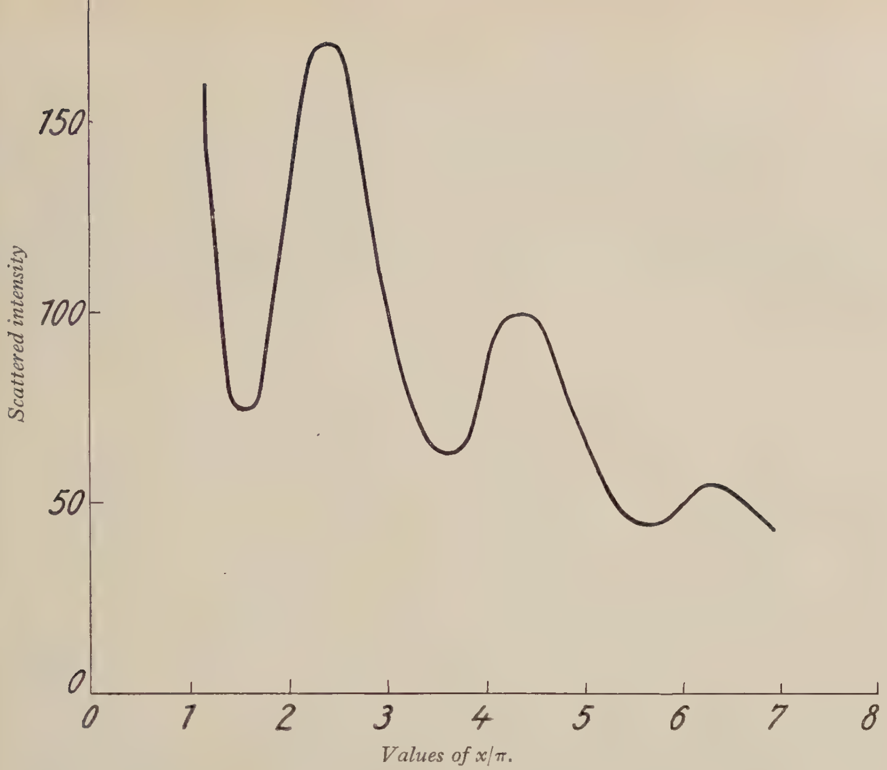

Fig. 4 *a*. Lower curve of Fig. 3, plotted on approximately the same scale as Fig. 4 *b*.

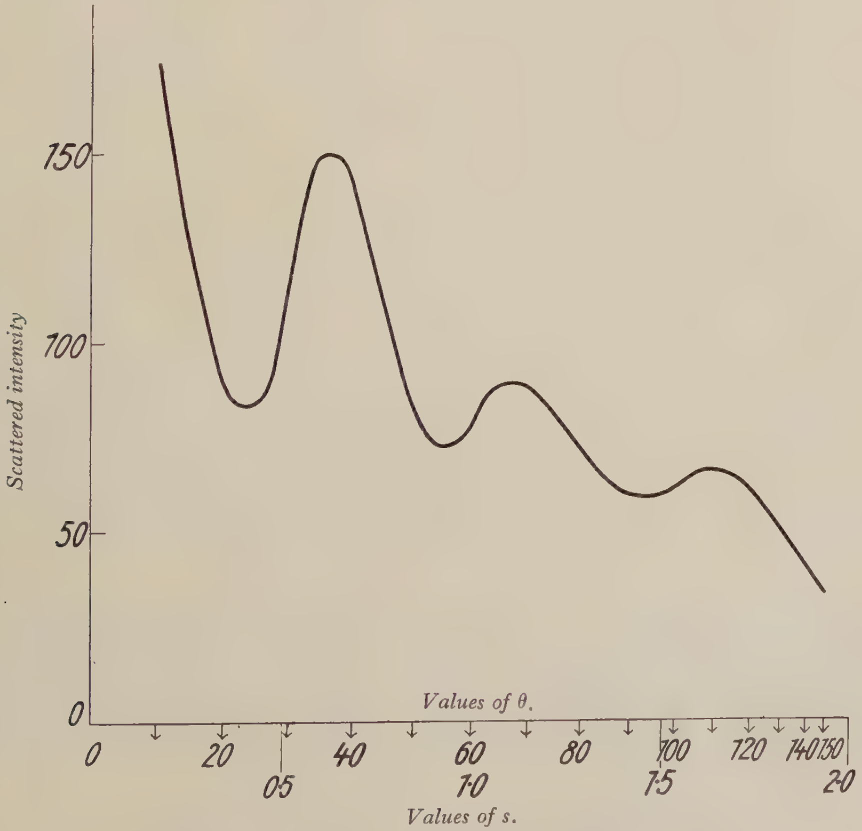

Fig. 4 *b*. Experimental scattering curve for C Cl_4.

The experimental scattering curve shows three minima and three maxima and the corresponding values of s were determined. The theoretical curve also shows three maxima and three minima at definite values of x, which can be read off from a drawing of appropriate size. The combination of any theoretical value of x with the corresponding experimental value of s constitutes a determination of the distance l between two Cl atoms. In the table this combination has been worked out. The second column contains the theoretical values of x/π, and to show the influence of the atomic size I have added in brackets the values which would be obtained without the correction. The third column contains the observed values of s and in the last column are given the values of l as calculated by the formula $x = ksl$. These six values differ from an average value $l = 2{\cdot}99$ A.U. by not more than ± 1 per cent. Remembering that, without the correction for the atomic size, l was found as 3·1 A.U. from the angle of the first maximum, it is seen that after all the finite dimensions of the atoms enter only as a correction amounting to not more than a few per cent. However, it must not be forgotten that in the case of CCl_4 interferences occur between radiations scattered by four atoms. If in other cases only three or even two atoms interact, the correction will be more important. Finally a comparison of the two curves in Figs. 4 *a* and 4 *b* shows that the maxima and minima in the theoretical curve are more pronounced than in the experimental curve. This is partly due to some experimental imperfections, but I think that the essential reason for this difference is due to the thermal motion of the atoms in the molecule which has not yet been considered.

Table

	x/π (theor.)	s (exper.)	l (A.U.)
1st Min.	1, 60 (1, 50)	0, 411	3, 00
1st Max.	2, 38 (2, 48)	0, 618	2, 97
2nd Min.	3, 60 (3, 42)	0, 93	2, 98
2nd Max.	4, 30 (4, 44)	1, 10	3, 01
3rd Min.	5, 70 (5, 50)	1, 46	3, 00
3rd Max.	6, 30 (6, 56)	1, 64	2, 96

So far we have always supposed the primary radiation to consist of X-rays. But we now know that electrons and material particles in general have to be treated according to the principle of wave-mechanics. Therefore it was of interest to repeat with material rays the experiments on the scattering by single molecules. According to de Broglie's fundamental equation, the wave-length λ associated with particles of mass m and velocity v is

$$\lambda = h/mv,$$

where h is Planck's constant, $6{\cdot}55 \times 10^{-27}$ erg-sec. For cathode-rays with a velocity corresponding to a potential difference of 30,000 volts the wave-length comes out to be $\lambda = 0{\cdot}071$ A.U. If therefore a beam of such cathode rays be scattered by CCl_4 molecules, we should expect a first interference maximum occurring roughly at an angle $\theta = 1{\cdot}6^\circ$ instead of $\theta = 36^\circ$, as observed with X-rays of the wave-length

1·54 A.U. Inspired by the results with X-rays, Mark and Wierl[*] carried out experiments of this type. They passed a beam of cathode rays perpendicularly through a stream of molecules and in the same case of CCl_4, for instance, the first two interference maxima were observed at angles corresponding to de Broglie's wave-length. The time of exposure was small, of the order of 1 minute. Mark and Wierl have calculated from their experiments that $l = 3{\cdot}14$ A.U. for CCl_4. They apply formula (2), treating the atomic scattering function as a constant, just as we did in the beginning for X-rays. For this reason their value for l must be compared with our former value $l = 3{\cdot}1$ A.U. Formula (2) should indeed be essentially correct except for the polarization factor $(1 + \cos^2 \theta)/2$ which, however, is of no importance for small angles. Moreover, the atomic scattering function ψ for electrons will not be the same as the atomic scattering function for X-rays. We can readily perform an approximate calculation, starting with Schrödinger's equation and assuming the electron energy of the primary beam to be large compared with the potential energy of the electron after entering the atom. From such a calculation it follows that in the case of electron scattering ψ will also have the property (in common with the scattering function for X-rays) of decreasing markedly with the increasing angle[†]. The correction will therefore be similar to the correction in the X-ray case.

A type of experiment which has not yet been performed and which seems worth trying is the scattering of atoms by single molecules in order to detect interferences of the scattered atoms[‡]. As the de Broglie wave-length involved for a beam of Hg atoms, for instance, moving with a velocity corresponding to their average thermal motion at ordinary temperature, is roughly 0·1 A.U., a possible first maximum for the scattering by CCl_4 molecules could be expected at an angle θ of about 2°. This is merely a suggestion, however, and is open to criticism in its details, though not, I think, in its general character.

The case of CCl_4 is so far the only case which has been more thoroughly discussed with respect to the influence of the atomic scattering function and even this only for X-ray scattering. Several other molecules, however, have already given interference maxima and minima as well with X-rays as with cathode-rays. The discussion of the results has yielded results of some interest, even though the variation of ψ has been neglected.

The photograph of the interferences for CCl_4 having been obtained, it was thought interesting to see if really, as was to be expected, the maxima and minima would become less pronounced for molecules in which only 3 or even 2 atoms could give a strong enough radiation to interfere. To this end the scattering was observed for the molecules $CHCl_3$, CH_2Cl_2 and CH_3Cl[§]. Decreasing the number of Cl atoms in the molecule indeed flattened the maxima, and for CH_3Cl no interference maximum could be observed. At the same time it was found that the first maximum shifted very appreciably to smaller angles with decreasing number of Cl atoms. This means that the distance between the Cl atoms increases if a Cl atom is replaced by an H atom. It is by no means improbable *a priori* that van't Hoff's tetrahedron becomes irregular if the atoms connected with the central C atom are different, and the experiments show that this is indeed the case. Moreover, the same conclusion is supported by the comparison of the dipole moments for the chlorine-substituted methanes*. The advantage here is that the magnitude of the change in distance can be measured absolutely.

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[*] H. Mark and R. Wierl, *Naturwiss.* **18**, 205 (1930).

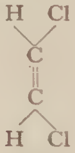
[†] Experiments of H. Mark and R. Wierl, *Zeit. für Phys.* **60**, 741 (1930) support this theoretical result.

[‡] The interference of molecular rays reflected by a crystal has been obtained by J. Estermann and O. Stern, *Zeit. für Phys.* **61**, 95 (1930).

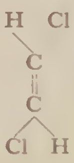
[§] P. Debye, L. Bewilogua and F. Ehrhardt, *Sächs. Akad. Ber.* **81**, 29 (1929).

The molecule CH_2Cl_2 was the first instance in which it was shown that two atoms are enough to give an interference maximum which can be detected experimentally. From this and from the similar case of CS_2 I concluded that one was justified in saying that any distance in a molecule could be measured interferometrically, provided only that two atoms containing enough electrons to give a relatively large scattering effect are situated or can be substituted one at each end of the distance to be measured. From recent experiments of Mark and Wierl it seems to follow that in the case of cathode-rays the conditions for this kind of measurement are still more favourable than for the X-ray case.

The above considerations were first applied to detect a difference in scattering between the two isomeric dichlormethylenes†, which in organic chemistry are represented by the two formulae



cis

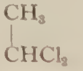


trans

The interference maxima of the first and second order were photographed. As was to be expected from the chemical formula, the cis-compound (boiling at 60° C.) was the one for which the first interference maximum occurred at the larger angle, indicating the smaller distance between the two Cl atoms. A calculation similar to that discussed for CCl_4 yielded for the two distances in the two isomeric molecules

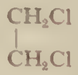
$$l_{\text{cis}} = 3{\cdot}6 \text{ A.U.} \quad \text{and} \quad l_{\text{trans}} = 4{\cdot}1 \text{ A.U.}$$

Another application of the principle was made for the two isomers ethylidenechloride and ethylenechloride:



$$\begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array}$$

and



$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

Here also interference maxima of the first and second order were found. The first 1, 1-compound shows its first interference maximum at a larger angle than the second 1, 2-compound. The calculated distances between the Cl atoms are

$$l_{1,1} = 3{\cdot}4 \text{ A.U.}, \quad l_{1,2} = 4{\cdot}4 \text{ A.U.}$$

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* R. Sänger, *Phys. Zeit.* **27**, 55 (1926).

† P. Debye, *Phys. Zeit.* **31**, 142 (1930).

They agree with what is to be expected from the chemical formulae; for if the two Cl atoms are connected with the same C atom, we should expect the smaller distance. However, the 1, 2-compound calls for a more thorough discussion. In this case from the fact that no isomers of the cis-trans kind have been detected in organic chemistry, the conclusion has been drawn that the two parts of the molecule have the possibility of free rotation around the bond C–C. From the scattering experiment it seems that a really free rotation does not exist; for otherwise the gas would have contained a mixture of molecules with very different distances between the Cl atoms and the interference maxima could not have been so pronounced as they were. I have been inclined to draw the conclusion from the scattering experiments that an equilibrium position exists, which is similar to the structure of the trans-isomer in the case of the double bond. As to the finite dipole moment which has been observed for the 1, 2-compound* it can be explained by the thermal oscillations of the two parts of the molecule about their equilibrium position and around the C–C bond. The temperature variation of the moment which follows from this supposition seems indeed to exist†. Wierl has recently observed the scattering of cathode rays by the same molecules‡ and has also found the interference maxima mentioned above. In particular, from the fact that the maximum of the second order observed for the 1, 2-compound occurs at a smaller angle compared with the first than in a straightforward case like CCl_4, this author is led to believe that not one but two equilibrium positions exist, comparable in their structure with the two cis-trans-isomers. He explains the effect of the shift of the second maximum (which we also observed with X-rays) by a 50–50 per cent. superposition of two theoretical scattering curves for the two kinds of molecules. As in this calculation no account has so far been taken of the influence of the atomic scattering curve, neither of the two suppositions can be said to be proved. I should like, therefore, to postpone a definite conclusion. However, it is certain that very soon the discussion of the experiments on scattering will give a definite answer to the problem of free rotation.

The number of other questions being treated by the scattering method, with X-rays as well as cathode-rays, is by no means small. Although my account has been far from complete, I hope that I have been able to convince you that the new method is promising enough to deserve your attention.

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* W. J. Williams, *Zeit. für phys. Chem.* A, **138**, 75 (1928).

† According to a remark of A. Eucken, about experiments carried out in his laboratory by L. Meyer, in *Molekulare Dipolmomente und ihre Bedeutung für die chemische Forschung, Fortschritte der Chemie, Phys. und phys. Chemie*, Bd. 20, Heft 5, S. 65.

‡ R. Wierl, *Phys. Zeit.* **31**, 366 (1930).

REVIEWS OF BOOKS

Differential Geometry of Three Dimensions, by C. E. Weatherburn. Vol. II. Pp. xii + 239. (Cambridge University Press.) 12*s*. 6*d*. net.

This volume is a continuation of the useful text-book, on the same subject, published by the author three years ago, the treatment being based on the systematic use of vector methods. Whatever views may be entertained as to the present-day effectiveness of these methods as an instrument of research, their conciseness and elegance frequently make strong appeal to students, and there is much to be said for their introduction at an early stage in the teaching of differential geometry. The new volume resumes and considerably expands the discussion of differential invariants begun in the first volume, and there are chapters on families of curves on a surface, families of surfaces, ruled and Weingarten surfaces, and curvilinear congruences; and two chapters deal with the deformation and application of surfaces. There is a short account of Levi-Civita parallelism. A large part of the book is derived from the author's own published papers, many sections of which are reproduced with little alteration other than a certain amount of rearrangement. This origin of so substantial a proportion of the matter of the book inevitably gives it a rather specialized character. It is written with great clearness and is provided with useful sets of examples, and the young geometer, as well as many other readers, will find it a handy means of getting rapidly into contact with an interesting range of recently published work.

G. S. L.

Einführung in die Wellenmechanik, von Louis de Broglie. Pp. iv + 221. (Leipzig: Akademische Verlagsgesellschaft m.b.H.) Br. R.M. 11: Geb. R.M. 13.80.

This translation into German of a French manuscript of Prof. L. de Broglie presents the subject of wave mechanics as a development of classical and relativity theories, gives an account of some of the experimental work which the new ideas have inspired, and discusses the new views which arise out of the modern departures from the older theories.

The opening chapters are concerned with the classical mechanical and wave theories, especially with the principles of Hamilton and Fermat. These principles and their relation to one another are essential in the new theory and the reader will find the subject very concisely and clearly treated.

The modern atomic theory requires the physicist to be well grounded in the theory of wave motion. In the older quantum theory he was called upon to study the details of orbital motion, now he must be familiar with wave trains and wave groups. These subjects are treated in the early chapters and the reader will find here an introduction to them or a reminder of many points that it is easy to forget.

The experimental side is briefly treated in chapter VII, where the work of G. P. Thomson is examined in some detail and reference is made to the pioneer work of Davisson and Germer, the purpose being rather to bring forward experimental evidence for the value of the new principles than to treat the experimental side of the subject. There are several concrete examples of the application of these principles which are very illustrative and add to the ease with which the argument can be followed.

The introduction to the book contains a discussion of the various attempts made by the author and others to explain the significance of the wave function.

There are difficulties associated with each view put forward, but the reader will probably conclude that these are least if the interpretation put forward by Bohr and eisenberg be accepted. This view is that the function is a probability function. As a onsequence of this point of view we are led to the uncertainty relations which are regarded s the expression of a physical principle of the first importance. Bohr regards it as essential o the whole structure of physics and as one which will enable us ultimately to rid ourselves f illogical conceptions which have grown up in the framework of the theory. We have ot of necessity to banish altogether our physical models, though we may need a new esign, and there are new workers who are so modest as to believe that their theories may erely remove the rust of the old ones and start them working again. But, whatever the utcome, the reader will find in this book a very attractive presentation of this important rinciple.

The difficulty of presenting in one volume the treatment by means of matrices as ell as the other treatment is liable sometimes to lead to the view that there are two new heories. The introduction of matrices very briefly in the last chapter should help to emove this misconception.

The appearance of a book by the author of an important theory is bound to be an vent of importance in the literature of the subject, and in this case the book is particularly elcome on account of the lucidity of the exposition.

X-Rays, by B. L. Worsnop. Pp. ix + 102. (London: Methuen & Co.) 2*s*. 6*d*.

This series of handy volumes, which Dr Worsnop very ably edits, does, in the language of the prefaces, "fill a long-felt want." It is a pleasure to find writers who can, clearly and concisely, produce an account of some corner of modern physical science which shall be thorough, interesting, not too condensed, nor yet overloaded with detail. Dr Worsnop's volume on X-rays fulfils most of these conditions. In the ninety-five pages at his disposal he discourses admirably on early experiments, X-ray spectroscopy, scattering, emission and absorption, photo-electrons and direct reflection, refraction and diffraction. His book is to be commended, and our only criticism is that Dr Worsnop has perhaps not fully considered the difficulty of getting a quart into a pint pot.

A. F.

The Microscopical Examination of Coal, by Clarence A. Seyler, B.Sc., F.I.C., assisted by W. J. Edwards, Department of Scientific and Industrial Research. Pp. vi + 67, with 17 plates. (London: H.M. Stationery Office.) 2*s*. 6*d*.

This is an account of the methods employed and the results obtained in a microscopical examination of coal, the aim of which is to determine the botanical nature of the original material and the nature of the physical and chemical changes which accompanied its transformation into coal, and to correlate this information with the coking and other properties of the surviving material.

First is given a method of preparing thin sections of coal for examination by transmitted light; then, the author has improved a method, based on metallographic practice, of polishing and etching flat surfaces of coal so as to bring out plant structures previously unrecognized; and there is a full description of a simple photomicrographic apparatus, particularly in its application to photography by vertical illumination. The excellence of the photographs testifies to the manipulative skill with which this work has been carried out.

The report is quite a good introduction to the study of the micropetrology of coal. It is informative and readable, and amazingly cheap.

M. T.

Recent Advances in Plant Physiology, by E. C. BARTON-WRIGHT, M.Sc. Pp. xii + 352. (London: J. & A. Churchill.) 12*s*. 6*d*.

Messrs J. & A. Churchill are publishing a series dealing with recent advances in various branches of modern science. There is a real need for such a series, the members of which shall treat their subjects adequately and in detail, with critical knowledge of and full references to original literature, but shall, at the same time, be produced at prices which do not put too great a strain upon the pocket of a student. So far, the series has been concerned with subjects mainly of medical interest, but Mr Barton-Wright's monograph makes an appeal to an audience whose interest is more purely scientific than that of the medical man.

Mr Barton-Wright, as was necessary if the volume was to be kept within moderate limits, makes but a selection from a large range of topics, and it so happens that his chapters include much that is of interest to the physicist. Soil and water relations, transpiration and allied subjects, carbon assimilation, nitrogen metabolism, respiration and the physiology of growth—these are Mr Barton-Wright's chapter headings, and serve to show the scope of his book. His treatment of these topics illustrates very clearly the change which is coming over those aspects of plant physiology which immediately concern the physicist. It is but a few years since the late Sir Francis Darwin remarked that the botanist concerned with a problem having physical bearings was wont to lose himself in a maze of suctions, pulls, osmotic pressure, capillarity, *vis a tergo*, tensile strengths and the like. This is still evident, but it is gradually disappearing, and we hear less and less of the very unphysical arguments which were once only too common.

Mr Barton-Wright gives a thoroughly interesting account of the transpiration problem, but it would have been better had he reminded his readers that some of the difficulties attendant on the use of the coefficient of relative transpiration—the ratio of the transpiration rate per unit area of the plant to the evaporation rate per unit area of some form of evaporimeter—might disappear if a certain purely physical fact were borne in mind, namely that the evaporation from a water surface of moderate dimensions is proportional not to the area A, but to $A^{3/4}$. Failure to recognize this fact has led to much confusion in the reduction of transpiration observations.

Mr Barton-Wright's book will prove of real service to students of botany, and physicists interested in the natural sciences will find many matters of interest in the chapters dealing with soil and water relations, transpiration and the physiology of growth—in particular there is room for much interesting work in the analysis of growth-curves (pp. 329 *et seqq.*), the study of which is exciting great interest at the present time.